A STABILITY STUDY OF COMPLEXES FORMED BY A METALIZABLE POLYPROPYLENE DYE

A THESIS

Presented to

The Faculty of the Graduate Division

by

Rick Anthony Porter

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Textiles

Georgia Institute of Technology

July, 1966

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Chairman

Date approved by Chairman: 27 July 1966

ACKNOWLEDGMENTS

The author is grateful to the Celanese Corporation of America for the financial aid which it has extended over the past year, and to Dr. James L. Taylor for his support and assistance in securing this fellowship.

The author wishes to express his appreciation to Dr. Ulrich Meyer for the suggestions which he has offered, and to Professor Raymond K. Flege, Dr. James A. Knight, and Dr. Robert F. Johnson for their service on the reading committee.

Special thanks are extended to the author's advisor, Dr. Johnson, for his enthusiastic support and for his assistance in selecting a topic for study. The author also wishes to acknowledge the effort exerted by Dr. Taylor and Dr. Johnson over the past year to acquire the laboratory facilities used in this research.

Finally, the author wishes to express his appreciation to his wife, Sylvia, for her encouragement and assistance in the preparation of this thesis.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

SUMMARY

Commercial acceptance of polypropylene fiber has been hindered by its susceptibility to degradation by ultraviolet radiation and its inability to be dyed by conventional methods. One method which produces a dyeable fiber is based upon incorporation of an organometallic ultraviolet radiation stabilizer. Disperse dyes are used which form an insoluble coordination complex with the metal present in the radiation stabilizer.

Dyes used in a mixture, which maintain a constant hue during the dyeing operation, may be referred to as being compatible. Tests have been devised for estimation of the compatibility of metalizable disperse polypropylene dyes when applied in a mixture. However, the compatibility of a few of these dyes is incorrectly assessed by these tests. A dye which is assessed to be compatible, yet is not, may be said to exhibit blocking.

The purpose of this research was to investigate some of the fundamental properties of the blocking phenomena as they apply to the polypropylene metalizable disperse dyeing system, in which the metal donor was an organonickel ultraviolet radiation stabilizer. An equilibrium model for the dyeing system was proposed and relationships, consistent with this model, which would aid in the study of blocking were obtained. On the basis of this model, it was shown that variables unique to the metalizable dispersed dyeing system were the rate of formation of the dye complex, the solubility of the dye complex, and the stability of the dye complex in the fiber phase.

The experimental part of this thesis consisted of measurement of the stability of the complex formed by a metalizable disperse dye. It was assumed that the fiber phase could be simulated by 2,2,4-trimethylpentane. The dye investigated was 6-ethoxy-2-(2-hydroxy-4-anilinophenylazo)-benzothiazole.

In 2,2,4-trimethylpentane saturated with water, the dye formed a 1:1-complex with nickel-(II). However, it was shown that the 2:1-complex does exist in N,N-dimethylformamide.. Reasons that the 1:1-complex is not formed in anhydrous 2,2,4-trimethylpentane were discussed.

It has been shown that the measurement of over-all stability constants may not be made in anhydrous 2,2,4-trimethylpentane. However, in this media, stability of a complex involved in a replacement reaction may be measured relative to a reference complex. The ultraviolet radiation stabilizer, di-[o,o'-bis-(p-1,1,3,3-tetramethylbutylphenol) monosulfide] nickel-(II), was chosen as the reference complex. The stability of the 2:1-dye-metal complex relative to the ultraviolet radiation stabilizer complex is equal to the equilibrium constant for the following reaction:

$$2\left(\begin{matrix}\text{Dye}\\ \text{ligands}\end{matrix}\right) + \begin{matrix}\text{Ultraviolet}\\ \text{radiation}\\ \text{stabilizer}\end{matrix} \rightleftharpoons \text{Dye complex} + 2\left(\begin{matrix}\text{Ultraviolet}\\ \text{radiation}\\ \text{stabilizer}\\ \text{ligands}\end{matrix}\right)$$

The value of this equilibrium constant has been measured for the species in question in anhydrous 2,2,4-trimethylpentane. Using the assumptions that activity coefficients of all species were unity and that no mixed dye-stabilizer complex or 1:1-dye-metal complex was formed, the calculations were made from spectral data. Values were obtained at 13 wave lengths and were from 0.00095 to 0.0250.

CHAPTER I

INTRODUCTION

History of Commercial Polypropylene Fiber

In 1955 Natta and Ziegler patented the first process for production of isotactic polypropylene. The isotactic polymer produced was highly crystalline and had good fiber forming properties. The low cost of the monomer made it an attractive raw material for fiber production. Some other advantageous properties of polypropylene fiber were low density, chemical resistance, and high strength in the presence of water. However, acceptance of polypropylene fiber has been hampered because of its low melting point, degradation by sunlight, and lack of dyeability.

The Problem of Melting Point

The melting point of crystalline polypropylene ($176^{\circ}C$) is an inherent problem. With respect to garment treatment, such as ironing and machine drying, the public is well educated in the extra care required of synthetic fibers. Therefore, melting point is not a severe handicap in this respect. The low melting point of polypropylene fiber is, however, a problem in prolonged heating operations associated with the now popular "durable press" finishes.

The Problem of Degradation by Sunlight

Many polymers are susceptible to degradation of the polymer chains by ultraviolet radiation. To minimize this difficulty, certain compounds may be added to the polymer melt before extrusion. These compounds fall into two basic categories, screening type stabilizers and reactive type

stabilizers (1). Screening type ultraviolet radiation stabilizers absorb highly in the region below 370 millimicrons, thereby preventing the polymer from absorbing the harmful radiation. The protective mechanism of reactive type ultraviolet radiation stabilizers is not entirely understood. However, in some way these compounds prevent free radical degradation of the polymer chain. These compounds are often referred to as antioxidants because aldehydes and ketones are intermediates formed in the process of degradation of polypropylene.

Polypropylene absorbs only a small amount of ultraviolet radiation, but is affected greatly by the radiation. For these reasons, reactive type stabilizers are used rather than screener types. Many of these reactive type stabilizers are organometalic coordination compounds.

The Problem of Dyeability

Much research has been done in attempts to piece dye polypropylene fiber (2) (3). These attempts have been hindered by the physical and chemical nature of the polymer. The compact nature of highly crystalline isotactic polypropylene makes diffusion of reagents into the fiber difficult. The hydrophobic nature of the polymer makes sorption of hydrophilic dyes difficult. The chemical structure of the pure polymer does not afford dye sites as found in natural and many man-made fibers.

Dyeing attempts have been made on both modified and unmodified polymer. The most successful dyeing of unmodified fiber has used non-charged dyes such as the disperse class, although many other classes of dyes have been investigated. The polymer has been modified to afford dyeability by use of a copolymer or by addition of certain compounds to the polymer melt before spinning of the fiber. Both copolymerization and graft

copolymerization of monomers which afford dye sites have been used. Additions to the polymer melt include cationic, anionic and organometalic compounds. The cationic compounds are typically polyamides, long-chain alkylamines, and nitrogen containing heterocyclic compounds. Addition of cationic compounds affords dyeability with anionic dyes of the acid class. The anionic compounds added to the polymer melt are typically poly-basic acids, alkylbenzene sulfonates, and acid anhydrides. Anionic compounds give dyeability with dyes of the cationic class. Organometallic compounds are typically aluminum, zinc, or nickel salts of fatty acids. Organo-aluminum residues from coordination polymerization initiators, and nickel alkylphenolates (refer to page 20) may also serve as organometallic dye sites. These metal-containing fibers are dyeable with disperse dyes (refer to page 20) capable of forming a coordination complex with the metal present.

Purpose of the Research

Some metalizable polypropylene dyes exhibit abnormal behavior when applied to polypropylene containing organometalic dye sites. The purpose of this research is to investigate some of the fundamental properties of these irregular phenomena, associated with the inclusion of nickel alkyl-phenolates in the fiber.

Description of the Metalizable Disperse Dyeing System

The incorporation of organometalic compounds into polypropylene, to afford dyeability with metalizable disperse dyes, offers a unique feature. That is, an organometallic ultraviolet radiation stabilizer may also serve as metal donor in dyeing operations. Nickel alkylphenolates are typical compounds which may serve this dual purpose.

The dyes used are non-charged oil-soluble compounds of relatively low molecular weights. These dyes diffuse readily into the polymer and are fixed by insolubilization.

The dyeing process consists of prescouring with a solution of a non-ionic detergent and sodium carbonate at approximately 100°C for twenty minutes. The scoured fabric is treated for fifteen minutes at 40°C in a bath containing six percent (percentages are based on the weight of the fabric) of an oil-soluble sodium alkylsulfonate and two percent acetic acid. The dye is pasted with an adequate dispersing agent and added to the bath. The bath is then heated to 90°C over a period of one hour and held for an additional 90 minutes at this temperature (4).

Problems Inherent in the Metalizable Dispersed Dyeing System

The dyeing of polypropylene, containing nickel alkylphenolate dye sites, has several distinct problems. The use of nickel alkylphenolate as the metal donor in the fiber necessitates removal of residual organoaluminum polymerization initiator (5). This is required since a mixture of nickel and aluminum dye complexes, having different spectral characteristics, would tend to dull the shade of the dyeing. The presence of metal ions, notably iron, in the dyebath might reduce the amount of dye available for fixation within the fiber by premature coordination. It has not been indicated by available literature that iron-(III) complexes cause dulling of shade. This might indicate that the complex formed is too large to diffuse rapidly into the fiber.

Another problem of this dyeing system is the necessity for a vigorous prescour. This is required because the presence of lubricating oils or waxy sizes, unevenly distributed on the fabric, will produce areas of

rapid diffusion of the dye into the substrate. This would result in skittery dyeing.

The use of the organometallic dyeing system has required the development of a completely new range of dyes. At present, relatively few dyes are available. This generally requires the use of mixtures of several dyes to obtain the desired shade. However, this is not unique since in commercial dyeing operations, mixtures of dyes are almost always used.

Dyes used in a mixture must give on-tone build-up to facilitate shade control. On-tone build-up may be defined as the maintaining of constant hue during the dyeing operation. Tests have been devised for estimation of the compatibility of metalizable polypropylene dyes for use in a mixture; however, the compatibility of some dyes is not properly assessed by these tests (6). A dye which is assessed to be compatible, yet is not, may be said to exhibit blocking. Blocking is defined as the preferential sorption of one dye in a dye mixture.

The purpose of this research was to investigate some of the fundamental properties of the blocking phenomenon as it applies to polypropylene dyeing.

Definition of the Problem

The Dyeing Mechanism and its Relation to Blocking

It has been discovered, empirically, that in general polypropylene dyes of the metalizable disperse type which have similar exhaustion rates, as a function of temperature, have good compatibly in dye mixtures (7). These rates are determined by indirect measurement of the amount of dye in the fiber with respect to the initial amount of dye in dispersion at the various temperatures using a constant dyeing time. This data is obtained

by first preparing standards of known concentration of dye in the fiber. This is accomplished by the use of equilibrium dyeings at concentrations varying from 0.1 to 1.0 percent. These standards of known concentration are then compared to a second set of dyeings made at a constant initial concentration at various temperatures ranging from 60° to 90°C for a given amount of time. The amount of dye in the fiber at this reproduced time is an indirect measurement of the rate of sorption of dye at the given temperature. Although the indirect rate measured is not the actual rate of sorption, it probably has more practical significance than the actual rate since it, in effect, averages the rates of sorption from time zero to the time of measurement. This is indicated in Figure 1 (refer to page 7).

The Mechanism of Dyeing - Equilibrium Discussion

It may be proposed that the dyeing of a synthetic fiber such as polypropylene, which is void of polar groups, with non-metalizable dispersed dyes would operate by a Nernst (partition) mechanism analogous to extraction. Although this simplified model does not take into account the crystalline and amorphous nature of the polymer, it does allow a more simplified interpretation of the system. The metalizable disperse dyeing system differs in one respect from this model. Once diffused into the fiber phase, the dyes coordinate with the nickel present forming a compound which is relatively insoluble in that phase. The molecular properties which produce this insolubility of the dye complex are not clearly understood. However, precipitation does occur, thus producing a pigmentation in situ.

The possibility of the presence of a third phase, in the form of a film of sulfonated alkyl compound (Naccolene A) adsorbed on the surface of

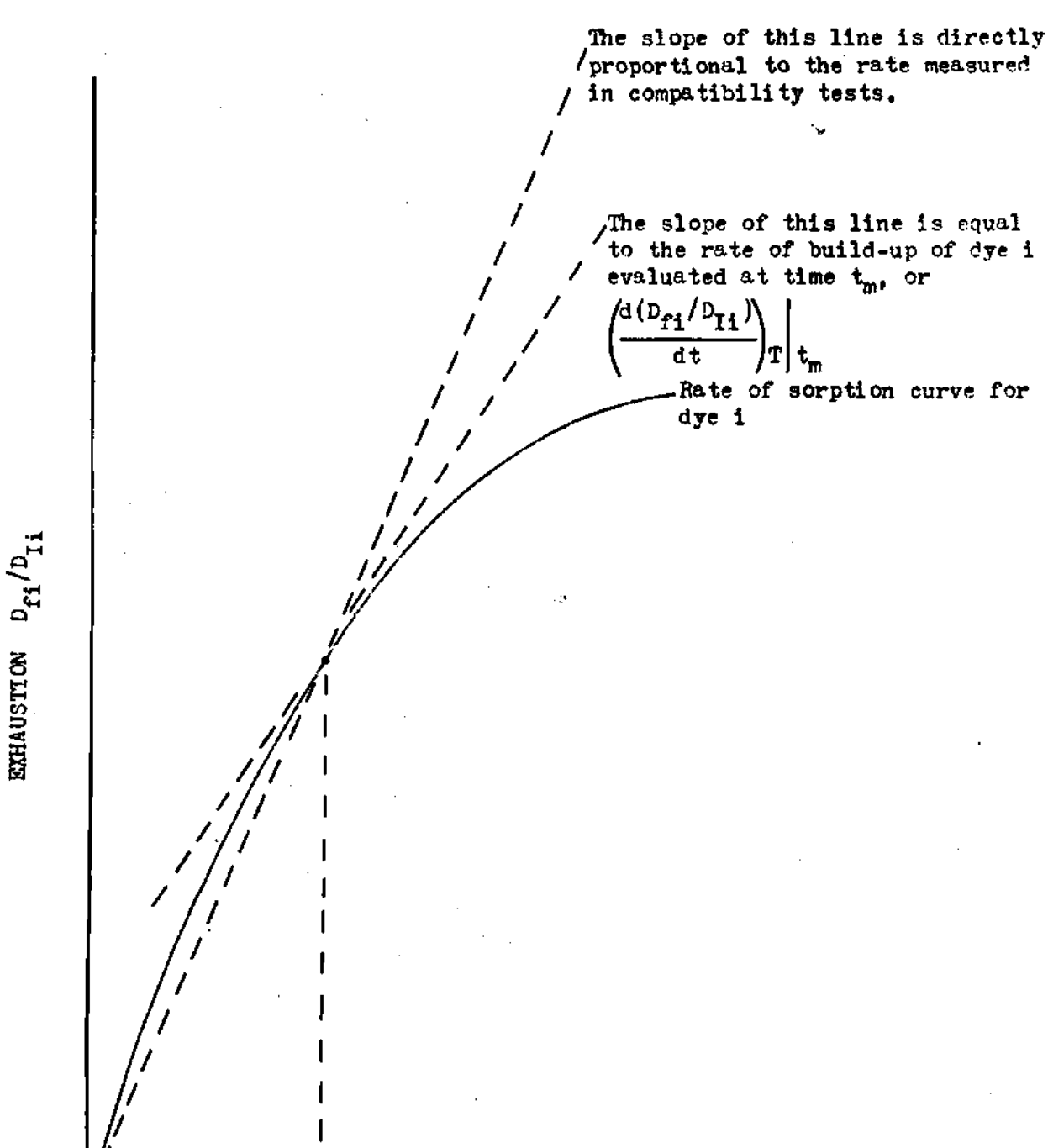


Figure 1. Graphic Representation of the Rate Measured in Dye Compatibility Tests.

the fiber, was investigated. The presence of such a modified hydrocarbon layer on the fiber might have a great effect on the dyeing characteristics of the fiber. Experimental work indicates that such an adsorption does not occur.

A fabric sample, with loose yarns removed, of Herculon (Type 40) nickel containing polypropylene fiber was scoured for 30 minutes at the boil in 500 milliliters of a solution containing 3.0 percent sodium carbonate and 0.3 percent Triton X-100, a non-ionic detergent. The scoured fabric was rinsed in five 500 milliliters portions of distilled water at 85°C. The rinsed fabric was dried to constant weight (24 hours) in a vacuum oven at 80°C and 30 millimeters mercury. The dried fabric was weighed (9.1785 grams), then worked for fifteen minutes at 40°C in 500 milliliters of a 0.1 percent acetic acid solution containing 0.8119 grams Naccolene A. The fabric was then centrifuged and weighed - 5.03 milliliters of inhibited solution was indicated. The wet fabric was again dried in a vacuum oven at the conditions mentioned above and weighed (9.1868 grams). Correcting for the presence of Naccolene A in the imbibed water, the weight difference upon treatment was 0.0002 grams, indicating that no significant adsorption of the compound had occurred.

The equilibrium sorption obtained by polypropylene dyes of the metalizable disperse type in fibers containing nickel alkylphenolates, corresponding to the partition-precipitation model would be controlled by two factors, the solubility of the complex in the fiber phase and the stability of the dye-metal complex.

Assuming that no mixed complexes of dye ligands and stabilizer ligands are formed and that activity coefficients are equal to unity, the

equilibrium reaction of polypropylene dyes with nickel alkylphenolate ultraviolet radiation stabilizer in the fiber phase may be represented as follows:

$$2(D_i) + (M(St)_2) \overset{Ki}{\rightleftharpoons} 2(St) + (M(D_i)_2)$$

An alphabetical glossary of abbreviations used throughout this paper is given in the appendix (refer to page 64).

Using the law of mass action, and letting parenthesises indicate concentration in moles per kilogram fiber, equation (1) is obtained.

$$K_i = \frac{(M(D_i)_2)\ (St)^2}{(M(St)_2)\ (D_i)^2} \tag{1}$$

If the aqueous solubility of all species is considered to be zero, and some amount of each dye i is considered to be precipitated within the fiber, from stoichiometric consideration of the system, the following relations are obtained:

$$(D_i) = (D_{Ii}) - (D_{Di} + D_{Ri}) \tag{2}$$

$$(M(St)_2) = \frac{D_S - D_{RT}}{2} \tag{3}$$

$$(St) = D_{RT} \tag{4}$$

$$(M(D_i)_2) = (M(D_i)_2)_{sat} = \frac{D_{Ri} - D_{fi}}{2} = \frac{(1 - FE_i)D_{Ri}}{2} \tag{5}$$

Substituting equations (2) through (5) into equation (1), the following is obtained:

$$K_i = \frac{2(M(D_i)_2)_{sat}(D_{RT})^2}{(D_S-D_{RT})(D_{Ii}-D_{Di}-D_{Ri})^2} \tag{6}$$

For the normal case in which the total initial amount of dye is less than the amount of dye sites, the value of D_{Di} at equilibrium will be approximately zero. Substituting this relation into equation (6) and rearranging, equation (7) is obtained.

$$\frac{(D_S-D_{RT})}{(D_{RT})^2} = \frac{2(M(D_i)_2)_{sat}}{K_i}\left(\frac{1}{D_{Ii} - D_{Ri}}\right)^2 \tag{7}$$

For convenience, equation (7) may be written as follows:

$$\frac{(D_S-D_{RT})}{(D_{RT})^2} = (C_i)^2 \cdot \frac{1}{(D_{Ii}-D_{Ri})^2} \tag{8}$$

where

$$C_i = \left(\frac{2(M(D_i)_2)_{sat}}{K_i}\right)^{\frac{1}{2}} \tag{9}$$

Noticing that the left side of equation (8) is the same for a mixture of any number of dyes, at equilibrium the following equations will be true.

$$\frac{(C_1)^2}{(D_{I1}-D_{R1})^2} = \frac{(C_2)^2}{(D_{I2}-D_{R2})^2} = \cdots\cdots = \frac{(C_w)^2}{(D_{Iw}-D_{Rw})^2} \tag{10}$$

Taking the square root of each equation in the above set of equations and inverting the set of equations, the equivalent relationship is obtained.

$$\frac{(D_{I1}-D_{R1})}{C_1} = \frac{(D_{I2}-D_{R2})}{C_2} = \cdots\cdots = \frac{(D_{Iw}-D_{Rw})}{C_w} \qquad (11)$$

From this equation, the values of D_{R2}, D_{R3}, ..., D_{Rw} may be obtained as a function of D_{R1}. These may be substituted into equation (12) to obtain the total amount of dye reacted as a function of D_{R1}.

$$D_{RT} = (C_1 D_{I1} - C_1 D_{I1}) + D_{R1} + D_{R2} + D_{R3} + \cdots\cdots + D_{Rw} \qquad (12)$$

Upon expansion and rearrangement of terms, the following expression is obtained.

$$D_{RT} = \left(\frac{D_{R1}-D_{I1}}{C_1}\right) \sum_{i=1}^{w} C_i + \sum_{i=1}^{w} D_{Ii} = \left(\frac{D_{R1}-D_{I1}}{C_1}\right) \sum_{i=1}^{w} C_i + D_{IT} \qquad (13)$$

Equation (13) rearranges to equation (14).

$$\frac{\sum_{i=1}^{w} C_i}{(D_{IT}-D_{RT})} = \frac{C_1}{(D_{I1}-D_{R1})} \qquad (14)$$

Squaring both sides of equation (14) and taking note of equations (8) and (10), the final result may be obtained.

$$\frac{(D_S-D_{RT})}{(D_{RT})^2} = \frac{\left(\sum_{i=1}^{w} C_i\right)^2}{(D_{IT}-D_{RT})^2} \qquad (15)$$

Using equation (15) and (8), the values of D_{RT} and D_{Ri} for each dye used is a mixture may be obtained, if C_i for each dye and the value of D_S is known. This may be done by solving the cubic equation obtained when equation (15) is expanded.

If the value of $(M(D_i)_2)_{sat}$ is also known, it may be used to calculate the amount of dye fixed on the fiber by use of equation (16).

$$D_{fi} = D_{Ri} - (M(D_i)_2)_{sat} \tag{16}$$

$$D_{fT} = D_{RT} - \sum_{i=1}^{w} (M(D_i)_2)_{sat} \tag{17}$$

The values of D_{Ii}, D_{Ri}, and D_{fi} thus obtained may be used to study any blocking which might occur between dyes in a mixture. The ratio of D_{fi} to D_{Ii} (which is the extent of exhaustion) should remain constant to facilitate estimation of dyes required to adjust the shade of a fabric; however, this is not absolutely required. For equilibrium blocking not to occur, the ratio of D_{fi} to D_{fT} must remain constant at each temperature at which the equilibrium is measured. This would require that the value of C_i be relatively independent of temperature.

The value of $(M(D_i)_2)_{sat}$ would also allow the estimation of the fixation efficiency of the various dyes used in a dyeing system. This would be done by the use of equation (18).

$$FE_i = 1 - \frac{(M(D_i)_2)_{sat}}{D_{Ri}} \tag{18}$$

The Mechanism of Dyeing - Kinetic Discussion

Commercial dyeing is predominantly a kinetically controlled process. Therefore, the kinetics of dyeing is an extremely important subject. Secondly, compatibility tests for polypropylene dyes are based on the rates of dyeing. For these reasons it is essential that kinetics of polypropylene dyeing be discussed.

Attempts to formulate an useable mathematical kinetic model for the polypropylene dyeing system has not been fruitful. However, a brief sketch of the relationships involved will be given.

The rate of sorption of dye i may be written as a function of some variables of the dyeing system.

$$\left(\frac{d(D_{fi})}{dt}\right)_S = f(k_{fi}, k_{si}, D_{fT}, D_S, D_{Ii}, \text{etc.}) \qquad (19)$$

The rate of desorption of dye i may also be written as a function of some variables of the dyeing system.

$$\left(\frac{d(D_{fi})}{dt}\right)_D = f'(k_{di}, k_{si}, D_{fi}, \text{etc.}) \qquad (20)$$

At equilibrium, the rate of sorption must be equal to the rate of desorption. From equation (19) and equation (20), equation (21) may be obtained.

$$f(k_{fi}, k_{si}, D_{fT}, D_S, D_{Ii}, \text{etc.}) = f'(k_{di}, k_{si}, D_{fi}, \text{etc.}) \qquad (21)$$

The above equation must be reducible to equation (1). The total rate of build-up of dye i may be expressed as the difference of the rate of sorption of dye i and the rate of desorption of dye i.

$$\left(\frac{d(D_{fi})}{dt}\right)_T = \left(\frac{d(D_{fi})}{dt}\right)_S - \left(\frac{d(D_{fi})}{dt}\right)_D \qquad (22)$$

$$= f(k_{fi}, k_{si}, D_{fT}, D_S, D_{Ii}, \text{etc.}) - f'(k_{di}, k_{si}, D_{fi}, \text{etc.})$$

Since D_{Ii} is not a function of time, the quantity measured in compatibility tests (Figure 1, refer to page 7) may be related to the quantity defined by equation (22).

$$\left(\frac{d(D_{fi}/D_{Ii})}{dt}\right)_T = \frac{1}{D_{Ii}}\left(\frac{dD_{fi}}{dt}\right)_T \qquad (23)$$

Thus, if two dyes are assessed compatible when dyed separately, the rates of build up must be equal over the temperature range involved. This may be expressed mathematically using equations (22) and (23).

$$\frac{1}{D_{I1}}\left[f(k_{f1}, k_{s1}, D_{f1}, D_S, D_{I1}, \text{etc.}) - f'(k_{d1}, k_{s1}, D_{f1}, \text{etc.})\right] =$$

$$\frac{1}{D_{I2}}\left[f(k_{f2}, k_{s2}, D_{f2}, D_S, D_{I2}, \text{etc.}) - f'(k_{d2}, k_{s2}, D_{f2}, \text{etc.})\right] \qquad (24)$$

For blocking not to occur, the rates of build up of the two dyes must in fact be equal, over the temperatures investigated, when applied in a mixture. This may also be expressed mathematically using equations (22) and (23).

$$\frac{1}{D_{I1}}\left[f(k_{f1}, k_{s1}, (D_{f1} + D_{f2}), D_S, D_{I1}, \text{etc.}) - f'(k_{d1}, k_{s1}, D_{f1}, \text{etc.})\right] =$$

$$\frac{1}{D_{I2}}\left[f'(k_{f2}, k_{s1}, (D_{f1} + D_{f2}), D_S, D_{I2}, \text{etc.}) - f'(k_{d2}, k_{s2}, D_{f2}, \text{etc.})\right] \qquad (25)$$

Subtraction of equation (24) from (25) would give an equation which must be true, over the temperatures involved, if a mixture of dyes which are assessed compatible are to in fact be compatible. The exact form of this equation can not be found unless the functional relationships f and f' are known. However, it is reasonable to assume that they will contain terms such as k_f,k_d, and k_s. Blocking will be dependent upon the value of k_f,k_d, and k_s and their temperature dependency.

In an effort to better understand the mechanism of dyeing of the polypropylene system, and to determine its influence on blocking phenomenon, measurements of rates of formation of dye complexes, equilibrium solubility of dye complexes in the fiber phase, and the stability of the dye complexes in the fiber phase are required. The latter is the aim of the experimental part of this thesis.

Choice of Solvent for Simulation of the Fiber Phase

Measurement of the stability of dye complexes formed within polypropylene presents many problems. Ideally, one should work with the polymer itself as the reaction solvent. However, this would require production of polypropylene films for use in optical measurement. This would necessitate the use of specialized equipment and skills, and would require a great deal of time. For these reasons a more easily handled substitute was chosen to simulate the polymer phase. A liquid aliphatic hydrocarbon, 2,2,4-trimethylpentane was chosen because it had chemical and physical properties which would effect complex stability similarly to the polymer. Secondary reasons for the use of 2,2,4-trimethylpentane were cost and the relatively high purity of the compound available. The use of such a non-polar reaction solvent introduced some unique problems to measurement of the complex stability.

Literature

The over-all reaction of a system involving one central metal ion (written M^{+p}) and two ligands (written $(L1)^{-q}$ and $(L2)^{-r}$) may be written as follows:

$$xM^{+p} + y(L1)^{-q} + z(L2)^{-r} \overset{B_{xyz}}{\rightleftharpoons} M_x(L1)_y(L2)_z^{\,xp-yq-zr}$$

Without indicating charges, and assuming activity coefficients equal to unity, the over-all stability constant of the $M_x(L1)_y(L2)_z$ complex is defined as follows (8):

$$B_{xyz} = \frac{[M_x(L1)_y(L2)_z]}{[M]^x[(L1)]^y[(L2)]^z} \qquad (26)$$

where brackets indicate molar concentrations.

When formed in non-polar medium, the stability of such a complex, as defined above, becomes undefined since the concentration of free metal ion approaches zero. An alternate method of obtaining stability constants (refer to page 21) has been investigated. This method is based upon the following equilibrium equation:

$$M(L1)_N + n(L2) \overset{K_{Nn}}{\rightleftharpoons} (M(L1)_{N-n}(L2)_n + n(L1)$$

$$K_{Nn} = \frac{[M(L1)_{N-n}(L2)_n][(L1)]^n}{[M(L1)_n][(L2)]^n} \qquad (27)$$

It has been indicated by Rossotti and Rossotti (9) that the value of K_{Nn} is related to the stability of the $M(L1)_N$ and $M(L1)_{N-n}(L2)_n$

complexes.

$$K_{Nn} = \frac{B_{1(N-n)n}}{B_{1NO}} \qquad (28)$$

This equation can be used to calculate the value of one stability constant if K_{Nn} and the other stability constant is known. A derivation has been used to show that, although $B_{1(N-n)n}$ and B_{1NO} can not be measured separately in non polar media, it is sufficient to make relative measurements of the stabilities of metal complexes of metalizable disperse polypropylene dyes and bis-alkylphenol monosulfides by using values of K_{Nn} (refer to page 21).

The method of measurement using equation (27) is referred to as replacement reaction technique. This method has been used in other investigations when the concentrations of ligands (L1) and (L2) are sufficiently high to assume that all of the central metal ion (M) is coordinated. Replacement methods have been used by Watters and DeWitt (10), (11) in studies of copper-(II) and nickel-(II) reacting with a mixture of oxalate ion and ethylenediamine using potentiometric techniques. Mixed tetra-(chlorobromo)-platinates (II) have been investigated by Dunning and Martin (12) using radiochemical analysis techniques. In every case the solvent system used has been water.

Newman and Hume (13) have elaborated on the theory of spectrophotometric techniques used in replacement stability measurements. However, the equations obtained require compliance with Lambert-Beer's Law, which was found not to apply for the species studied (refer to page 48).

To establish the composition of the complex formed, the method of continuous variations (14) was used. This method, first elucidated by Job, is one of the most widely used methods for determination of complex composition. A modified two-phase form of Job's method, described by Irving and Pierce (15), was used for determination of composition in an aliphatic medium. This was required since the dye ligand is soluble in aliphatic solvents, but not in water; and nickel ion is soluble in aqueous media, but not in 2,2,4-trimethylpentane.

CHAPTER II

PROCEDURE

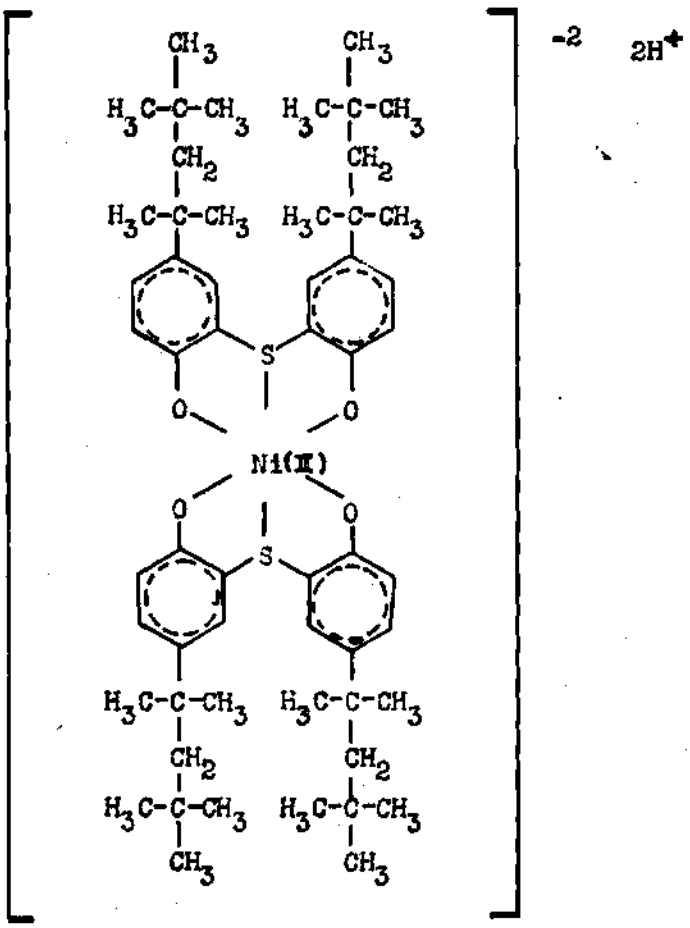
Method of Attack

Specific representative examples of a polypropylene dye and ultraviolet radiation stabilizer were selected from patent literature. These compounds, and most of their reaction products, were synthesized and purified, or purified from commercially available products. The spectral properties of these compounds were measured. Optical absorbancies of these compounds were then used to analyze for the concentration of the reaction species in solution, thus allowing indirect calculation of stability constants. Some difficulty in synthesis and rationalization of the structure of the dye complex was encountered.

Choice of Compounds for Investigation

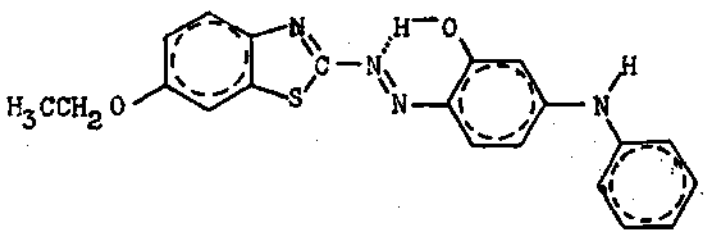
Metal-containing dyeable polypropylene fiber has been produced commercially in the United States by Hercules Powder Company and Reeves Brothers Company. Metal-containing ultraviolet radiation stabilizers for use in polypropylene fiber have been introduced by the Ferro Corporation. Ferro Corporation patents (16) indicate the structure of a suitable ultraviolet radiation stabilizer to be as indicated in Figure 2 (refer to page 20).

Patents obtained by the Hercules Powder Corporation indicate the use of such compounds may optically stabilize the fiber (17) and produce dyeability (18).



di-[o,o'-bis-(p-1,1,3,3-tetramethylbutylphenol) monosulfide] Nickel-(II)

Figure 2. Chemical Structure of a Commercial Ultraviolet Radiation Stabilizer.



6-ethoxy-2-(2-hydroxy-4-anilinophenylazo) -benzothiazole

Figure 3. Chemical Structure of a Commercial Polypropylene Dye.

Special metalizable dyes required by the metal-containing polypropylene fiber have been developed by Imperial Chemical Industries Limited, Ciba Company, Badische Anilin and Soda Fabrik, and by National Aniline (a division of Allied Chemical Corporation). Otto B. May Company has produced similar dyes, primarily for use with fiber containing aluminum (19). Patents (20) indicate the structure of a suitable polypropylene metalizable dye to be as shown in Figure 3 (refer to page 20). The structure of the possible complexes formed by this dye are discussed on pages 42 to 44.

Method of Indirect Stability Measurement

As discussed on page 16, the stability constants of complexes formed in 2,2,4-trimethylpentane can not be measured separately. For this reason, the use of replacement reactions is required. For the reaction of an ultraviolet radiation stabilizer such as di-[o,o'-bis-(p-1,1,3,3-tetramethylbutylphenol) monosulfide] Nickel-(II), which is a 2:1-complex, with a polypropylene dye such as 6-ethoxy-2-(2-hydroxy-4-anilinophenylazo)-benzothiazole in nonaqueous 2,2,4-trimethylpentane, the following equilibria may be proposed. (refer to page 9 and 16)

$$M(L1)_2 + (L2) \underset{\rightleftharpoons}{\overset{(K_{21})_{L1,L2}}{\rightleftharpoons}} M(L1)(L2) + (L1)$$

$$M(L1)_2 + 2(L2) \underset{\rightleftharpoons}{\overset{(K_{22})_{L1,L2}}{\rightleftharpoons}} M(L2)_2 + 2(L1)$$

The polypropylene dye is represented as the second ligand (L2), and the ultraviolet stabilizer is represented as the complex of the first ligand ($M(L1)_2$).

For these equilibrium reactions, if the activity coefficients are equal

to unity, the following equations apply.

$$(K_{21})_{L1,L2} = \frac{[M(L1)(L2)][L1)]}{[M(L1)_2][(L2)]} \qquad (1)$$

$$(K_{22})_{L1,L2} = \frac{[M(L2)_2][(L1)]^2}{[M(L1)_2][(L2)]^2} \qquad (2)$$

The over-all stability constant (refer to page 16) for the formation of the $M(L1)_2$ complex may be written as follows:

$$(B_{120})_{L1} = \frac{[M(L1)_2]}{[M][(L1)]^2} \qquad (3)$$

It should be noted that this stability constant is not a function of the second ligand.

As in equation (3), the stability of $M(L2)_2$ may be written as follows:

$$(B_{102})_{L2} = \frac{[M(L2)_2]}{[M][(L2)]^2} \qquad (4)$$

The stability constant of the mixed complex M(L1) (L2) may be represented as follows:

$$(B_{111})_{L1,L2} = \frac{[M(L1)(L2)]}{[M][(L1)][(L2)]} \qquad (5)$$

If equation (3) is divided into equation (5), and the similarity of the result to equation (1) noted, equation (6) is obtained.

$$\frac{(B_{111})_{L1,L2}}{(B_{120})_{L1}} = \frac{[M(L1)(L2)][(L1)]}{[M(L1)_2][(L2)]} = (K_{21})_{L1,L2} \qquad (6)$$

Likewise, if equation (3) is divided into equation (4), and the similarity of the result to equation (2) noted, equation (7) is obtained.

$$\frac{(B_{102})_{L2}}{(B_{120})_{L1}} = \frac{[M(L2)_2][(L1)]^2}{[M(L1)_2][(L2)]^2} = (K_{22})_{L1,L2} \qquad (7)$$

Equations (6) and (7) are merely proof of equation (28) in chapter I (refer to page 17), which is rewritten in the following altered form.

$$(K_{2n}) = \frac{(B_{1(2-n)n})}{(B_{120})_{L1}} \qquad (8)$$

Noting in equation (8) that the stability of the ultraviolet radiation stabilizer complex is independent of the dye ligand, it appears that the value of (K_{2n}) is a relative measure of the stability of any dye complex, since $(B_{120})_{L1}$ will have the same value in each case.

In general, any two stability constants may be obtained as some simple function of (K_{2n}). Since the stabilizer is unique in that it is the only compound which is necessarily present when dyeing polypropylene with metalizable dyes, it is natural that this complex be chosen as the "reference complex". Thus, the value of (K_{2n}) can be given as the "stability of the $(M(L1)_{2-n}(L2)_n)$ complex, relative to the stabilizer complex". Because the values of these "relative" stability constants might find use in the study of blocking phenomena, the relations which are involved in dye mixtures should be discussed.

For the previous discussion, in which $M(L1)_2$ was the ultraviolet radiation stabilizer, St may be substituted for (L1). Likewise for the dye (L2), D_i may be substituted for (L2). Making these changes, equations (6) and (7) may be rewritten as follows:

$$\frac{(B_{111})_{St,Di}}{(B_{120})_{St}} = (K_{21})_{St,Di} \tag{9}$$

$$\frac{(B_{102})_{Di}}{(B_{120})_{St}} = (K_{22})_{St,Di} \tag{10}$$

Likewise for the reaction of the stabilizer and a dye D_j, similar equations may be written.

$$\frac{(B_{111})_{St,Dj}}{(B_{120})_{St}} = (K_{21})_{St,Dj} \tag{11}$$

$$\frac{(B_{102})_{Dj}}{(B_{120})_{St}} = (K_{22})_{St,Dj} \tag{12}$$

For a mixture of any two dyes D_i and D_j (where $j \neq i$), equilibrium reactions between the two dyes may be written which are analogous to those for the reaction of dye and stabilizer. The reaction equilibrium may be indicated as follows:

$$M(D_i)_2 + (D_j) \underset{}{\overset{(K_{21})_{Di,Dj}}{\rightleftharpoons}} M(D_i)(D_j) + (D_i)$$

$$M(D_i)_2 + 2(D_j) \underset{}{\overset{(K_{22})_{Di,Dj}}{\rightleftharpoons}} M(D_j)_2 + 2(D_i)$$

In order to avoid unnecessary redundancy, D_i may be thought of as being (L1) and D_j may be thought of as being (L2). Thus, all of the derivations from page 21 to page 23 would apply, and equations (6) and (7) would be rewritten as follows:

$$\frac{(B_{111})_{Di,Dj}}{(B_{120})_{Di}} = (K_{21})_{Di,Dj} \tag{13}$$

$$\frac{(B_{102})_{Dj}}{(B_{120})_{Di}} = (K_{22})_{Di,Dj} \tag{14}$$

For any two dyes, D_i and D_j, equation (10) may be divided by equation (12) to obtain equation (15), and equation (9) may be divided by equation (11) to obtain equation (16).

$$\frac{(K_{22})_{St,Di}}{(K_{22})_{St,Dj}} = \frac{(B_{102})_{Di}}{(B_{102})_{Dj}} \tag{15}$$

$$\frac{(K_{21})_{St,Di}}{(K_{21})_{St,Dj}} = \frac{(B_{111})_{St,Di}}{(B_{111})_{St,Dj}} \tag{16}$$

Noting the fact that $(B_{102})_{Di} = (B_{120})_{Di}$ and $(B_{102})_{Dj} = (B_{102})_{Dj}$, (These terms are equal because they are merely different notations for the same compound.) and substituting these values in equation (14) and (15), equation (17) is the final result.

$$\frac{(K_{22})_{St,Di}}{(K_{22})_{St,Dj}} = \frac{1}{(K_{22})_{Di,Dj}} \tag{17}$$

From equations (13) and (16), because the mixed complexes are dependent

upon both species undergoing reaction, inequality (18) may be concluded.

$$\frac{(K_{21})_{St,Di}}{(K_{21})_{St,Dj}} \neq \frac{1}{(K_{21})_{Di,Dj}} \qquad (18)$$

In summation, it can be said that although it is impossible to measure the stability of the individual dye complexes formed in 2,2,4-trimethylpentane, the value of $(K_{22})_{St,D}$ is a measure of the stability of the dye complex "relative" to the stabilizer complex. Likewise, the value of $(K_{21})_{St,D}$ is a measure of the stability of the mixed dye-stabilizer complex relative to the stabilizer complex. Secondly, a tabulation of the values of $(K_{22})_{St,D}$ is sufficient to evaluate the equilibrium established between any two dyes, assuming no mixed dye complexes are formed. The stability of any mixed dye complexes formed between dyes used in a mixture must be investigated separately.

Synthesis and Purification of Reaction Products

The Quality of Chemicals used in Synthesis and Purification

Technical grade solvents, which had been distilled in a glass apparatus, were used for recrystallization and chromatographic separations. All materials used in synthesis were either reagent grade or technical material which was subsequently purified and its purity assessed. The melting points of recrystallized products were not corrected; and they were used only as an indication of the efficiency of the purification.

The nickel-(II) chloride used in synthesis of the ultraviolet stabilizer and in the two-phase Job diagram was reagent grade material. The water of crystallization was determined by drying the sample in a vacuum oven for three days at 80°C and 30 millimeters mercury to its yellow

anhydrous form. The final weight indicated the formula to be $NiCl_2 \cdot (2.9) H_2O$. This formula was used for calculation of all nickel concentrations. The water used in the two-phase Job diagram was redistilled in a glass apparatus. The 2,2,4-trimethylpentane used as the reaction solvent was technical grade material which had been dried over silica gel and distilled. The fraction from 97.5°C to 98.5°C was collected.

All the glassware used in the final measurement (volumetric flasks, pipettes, cells, etc.) were rinsed in distilled technical grade acetone. Distillation of the washing solvent was found to be necessary because traces of metal remained upon evaporation, and gave erratic results.

Synthesis of Stabilizer Ligand

The stabilizer ligand o,o'-bis-(p-1,1,3,3-tetramethylbutylphenol) monosulfide was synthesized as indicated in patent literature (20). The precursor to this compound, p-1,1,3,3-tetramethylbutylphenol, was purified from the technical grade product. This compound, commonly called octylphenol, contained approximately 90 percent of the monoalkylated compound. The pure compound can be isolated by recrystallization from n-heptane. The melting point of the compound purified by recrystallization is reported to be 84-85°C(21). The commercial compound was recrystallized four times approximately its own weight of n-heptane. Melting points of the needle-like crystals were taken. The melting points, ranges not indicated, were 60°,76°,82°, and 85°C for each recrystallization respectively. Purity was further assessed by gas chromatolgraphy, using the Perkin-Elmer 880 gas chromatograph with SE-30 silicone columns. The instrument was equipped with nitrogen as the carrier gas and hydrogen flame detection. The chromatogram was run from 100°C to 300°C at 10°C per minute. Heptane was used

as the injection solvent. The impure compound showed two major and several minor peaks; and the purified compound showed essentially one major peak.

Exactly 0.314 moles of the purified octylphenol, dissolved in 200 milliliters of carbon tetrachloride, was reacted with 0.157 moles of sulfur dichloride, dissolved in 12 milliliters of carbon tetrachloride, at 7°C with slow addition over a period of one hour. The reaction mass was stirred for an additional hour and allowed to react for 24 hours. The reaction mass was then washed twice with an approximately equal volume of distilled water, and 100 milliliters of petroleum ether (boiling point 30°C - 60°C) was added. The solution was cooled in a sodium chloride-ice mixture and the precipitate collected by filtration.

The reaction product was recrystallized four times from approximately twice its weight of n-heptane. The melting points of the colorless, translucent, rhombic crystals obtained were taken. The melting points, ranges not indicated, were 119°, 129°, 135°, and 138°C for each recrystallization respectively.

Synthesis of the Stabilizer Complex

Most of the stabilizer ligand synthesized, as described above, was used for synthesis of the stabilizer complex. The complex synthesis is described in the same literature as that of the ligand synthesis. A small sample of metallic sodium was weighed under ligroin in a weighing bottle with a tight lid. The sample of sodium was transferred from the weighing bottle to a small amount of absolute ethanol in a flask fitted with a drying tube. The volume of the solution of sodium ethoxide thus produced was measured, and the proportional amount required to form the monosodium salt of o,o'-bis-(p-1,1,3,3,-tetramethylbutylphenol) monosulfide was added

to an absolute ethanol solution of the latter.

The half-salt of the stabilizer ligand was added to an absolute ethanol solution of the exact amount of nickel-(II) chloride required to form the 2:1-complex. The complex was allowed to form for seven days. A yellow precipitate was formed and removed. The ethanol solution was evaporated to dryness in a rotary evaporator, and the solids dissolved in a minimum amount of warm n-heptane. Upon standing for one week, rhombic crystals of the monosodium salt of the stabilizer ligand precipitated. These crystals were removed and the solution evaporated. Traces of n-heptane which remained in the solids were removed after two days under vacuum at 0.7 millimeter mercury at room temperature. A single elemental microanalysis was performed on the green final product. The results of the analysis were carbon 71.35 percent, hydrogen 8.86 percent, oxygen 6.82 percent (by difference), sulfur 6.71 percent, and nickel 6.26 percent. The theoretical quantities of the elements present in the compound were carbon 71.56 percent, hydrogen 8.77 percent, oxygen 6.79 percent, sulfur 6.81 percent, and nickel 6.23 percent.

An explanation for the incomplete use of the half-salt of the stabilizer ligand in formation of the complex was that the yellow precipitate, which formed upon addition of the nickel chloride, was the anhydrous form of the latter. This loss of nickel ion might have been averted by working in an ethanol-water solvent. Although the reaction product was not recrystallized, its purity was indicated to be high. This was due to the vast difference in solubility of the stabilizer complex and monosodium o,o'-bis-(p-1,1,3,3-tetramethylbutylphenol) monosulfide in n-heptane at room temperature. The limiting factor in purification by this technique was that as

the concentration of the stabilizer increased, the viscosity increased until crystallization of the half-salt of the stabilizer ligand ceased.

Purification of the Dye Ligand

The dye ligand was purified from a commercially available product. This method was chosen rather than synthesis because it was hoped that a somewhat general purification routine might be discovered. This would facilitate purification of the other polypropylene dyes presently available.

Direct recrystallization was attempted in many solvents. The best of the solvents investigated were acetone, anhydrous ethanol, dimethylformamide, dioxane, and nitrobenzene; however, in no case did crystals form upon cooling. It was felt that the dispersing agent present in the commercial dye might be preventing crystal growth. Therefore, a method of removal of this compound was sought.

It was found that an aqueous dispersion of the dye could be partly broken, leaving the majority of the dispersing agent in an aqueous solution. This could be done in the following way. To an one gram sample of the dye dispersed in a liter of water, one gram potassium hydroxide, ten milliliters of acetone, and five grams potassium chloride were added. To this solution at 90°C, 1.5 grams of concentrated sulfuric acid was added to precipitate the dye. This technique occasionally gave good results; however, the rate of addition of acid, the temperature, and the rate of stirring had a great influence on the success of the precipitation and made reproducing results difficult.

A second method for precipitation of the dye from aqueous dispersion was investigated. To a two gram sample of the dye dispersed in a liter of

water, four grams of aluminum sulfate (octadecahydrate) was added. A solution containing one gram of potassium hydroxide was added to the dispersion at 60°C. The feathery precipitate of aluminum hydroxide formed allowed the solids, suspended in the water, to be removed by gravity filtration. Most of the dispersing agent remained in aqueous solution. The dye obtained by this technique was not used in further purification because separation of the dye from the aluminum hydroxide would have been difficult and extensive amounts of the aluminum complex of the dye might have been formed. This technique was, however, an excellent method for obtaining a sample of the dispersing agent used in the dye.

Concurrent with the work done on removal of the dispersing agent, work was performed on chromatographic estimation of the purity of the commercial dye. This was to be used for monitoring the purification of the dye. It was found that on paper and thin-layer chromatography, solvents which gave sufficiently low R_f values to perform separation also produced extensive tailing, thus preventing complete separation. It was found, however, that the dispersing agent which had been obtained and concentrated had substantially lower R_f values than the dye in ethanol solutions containing one to five percent water. The method of location of the dispersing agent was acid charring. This was performed by spraying the thin-layer plate, after development, with a five percent solution of sulfuric acid. The chromatogram was then heated in an oven for thirty minutes at 150°C. The results of such a chromatogram are shown in Figure 4 (refer to page 33). The adsorbent used was Aluminum Oxide G (E. Merck A. G. Darmstadt); and the eluent was 98 percent ethanol - 2 percent water. In general, better separations were obtained with lower water contents.

This suggested that chromatography might readily separate the dispersing agent from the colored compounds present in the commercial dye. It was found that the dye mixture could be separated by column chromatography using aluminum oxide as the adsorbent and ethanol-water mixtures as the eluent. Figure 5 (refer to page 33) is a graphic representation of such a separation. The column was loaded with a saturated solution of the commercial dye mixture in absolute ethanol. Elution with absolute ethanol was continued until all of the first component, a blue compound, was collected. The eluent was then changed to 95 percent ethanol-water solution and the second component, a red compound, was obtained. The final component, which was a small quantity of an orange compound, was removed using 50 percent ethanol-water. It should be noted that a small quantity of a blue component, which proved to be similar to the first component obtained, preceded the red component after aqueous ethanol was added to the column.

Addition of sulfuric acid and potassium hydroxide to the compounds, obtained by chromatographic separation of the dye mixture, showed that the red and blue components were forms of the same compound. The data obtained for addition of acid and base to the components of the mixture which were isolated is represented in the chart in the upper portion of Figure 6 (refer to page 34).

Addition of acid and base to the pure red component, followed by column chromatography, showed that no blue component of low retention time was formed. These chromatograms, depicted in Figure 6, indicate that the red and blue components separated from the dye mixutre are not merely different protonated forms of the same compound. The blue component could have been a protonated form of the red component and not have been

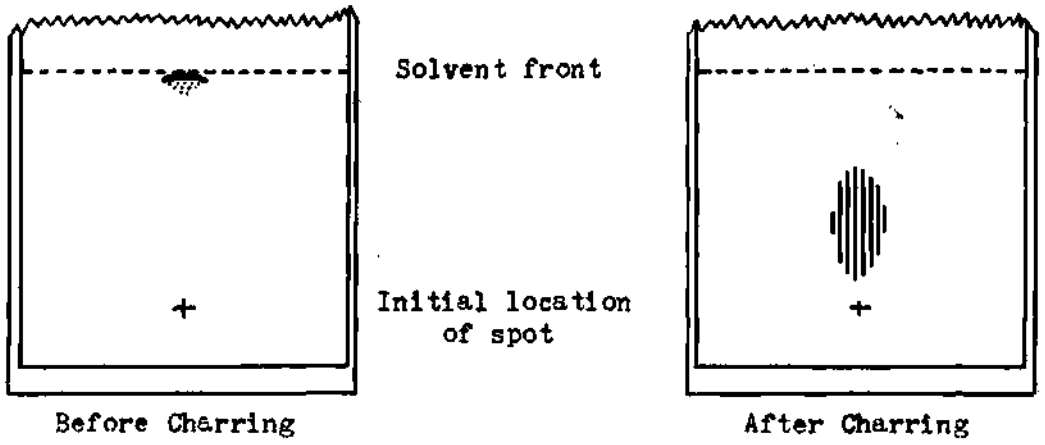


Figure 4. Location of Dispersing Agent on Thin Layer Chromatogram by Acid Charring.

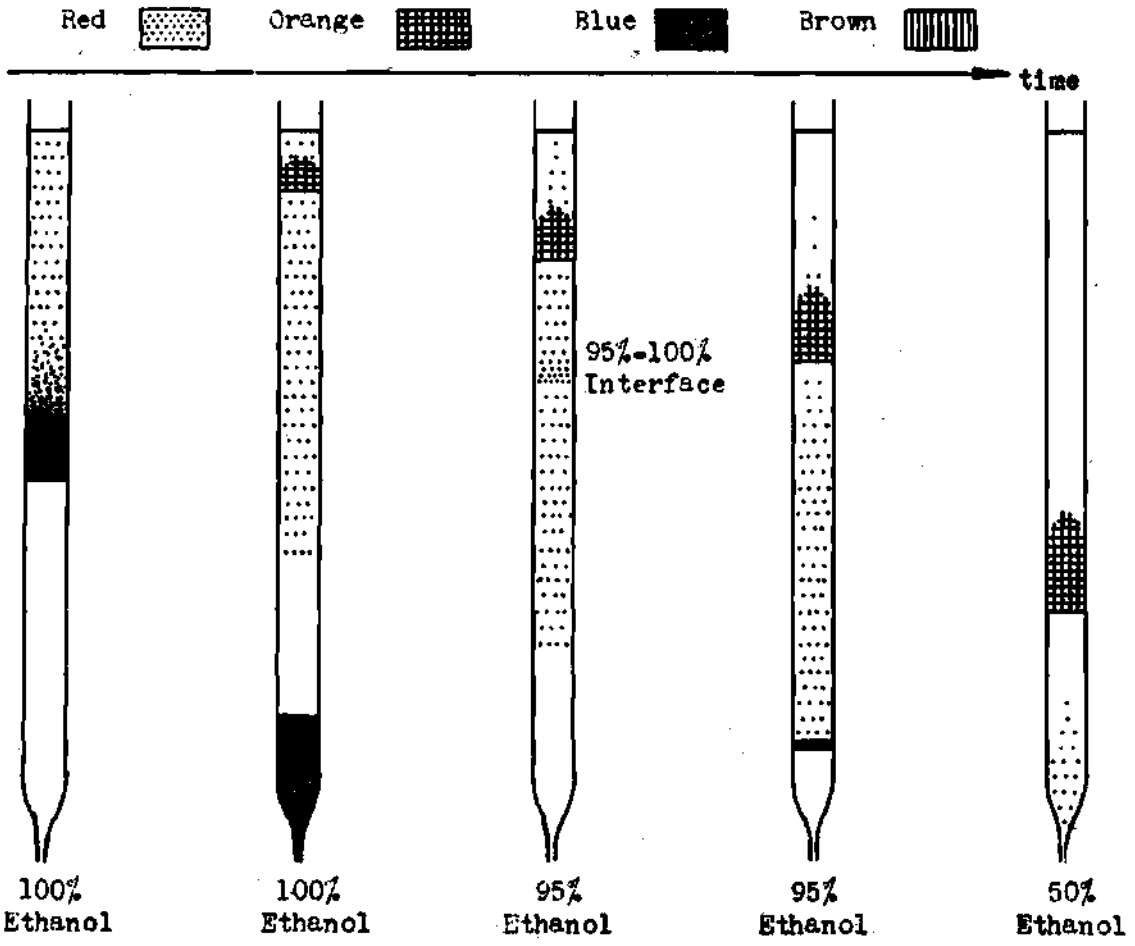


Figure 5. Separation of the Compounds Present in the Commercial Dye.

	Addition of Acid	Compound Isolated From Column Chromatography		Addition of Base
	←	Color	Order	→
	Violet	Orange	Third	No change
	Indigo Blue	Red	Second	Reddish Purple
Indigo Blue	Red	Blue	First	Reddish Purple

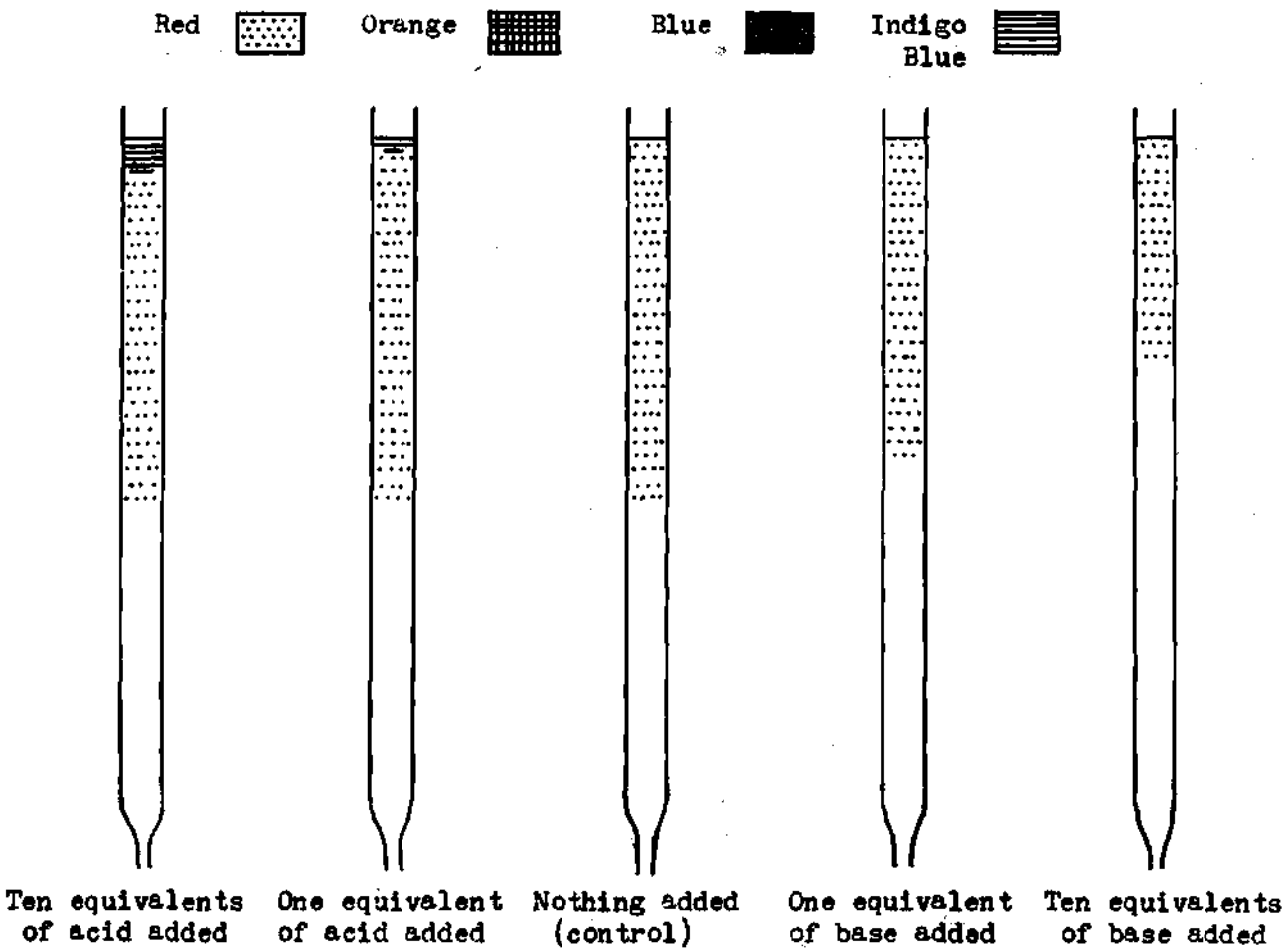


Figure 6. Identification of the Red Compound Isolated by Column Chromatography From the Commercial Dye.

ascertained as such because the compound produced upon addition of base to the red compound was reddish-purple and might have masked the presence of a blue intermediate compound. However, a blue component of relatively low retention time was produced by addition of metal salts to ethanol solution of the red component.

The blue region which preceded the red component, after addition of aqueous ethanol, gave color changes upon addition of acid and base which were identical to the colors obtained by addition of acid and base to the first blue component. This blue compound was not formed if aqueous ethanol was added to the pure red component obtained by anhydrous chromatography. However, the blue compound was formed in aqueous ethanol in the presence of aluminum oxide.

Apparently the red component, isolated by chromatography, was the dye ligand in the form indicated in Figure 3 (refer to page 20), since its color remained unchanged when in a solution buffered to approximately neutrality. The reddish-purple compound formed by addition of potassium hydroxide to the red component was undoubtedly the potassium salt of the hydroxy group present in the dye. The indigo-blue compound produced by addition of acid to the red compound was the salt of either the amino group or the heterocyclic nitrogen.

It was found that the dye obtained by the column chromatographic technique, described on page 32, could be recrystallized from absolute ethanol to give a product of high purity. The product contained none of the blue complex formed by reaction with the adsorbent which was present, however, in the mother liquor. Crystallization was performed in the following way. The solution obtained from chromatography was evaporated to

dryness in a rotary evaporator and dissolved in an ample amount of absolute ethanol. This solution was filtered through Celite (diatomite filter-aid, Johns-Manville) to remove suspended particles of alumina. The Celite was first checked by chromatography for reaction with the dye; no reaction was indicated. Most of the ethanol was removed from the filtrate, the solution heated, and sufficient ethanol added to eliminate the appearance of particles on the sides of the container when shaken. The crystallization was completed by cooling.

The reddish-brown, octahedral-shaped crystals obtained melted at 238°C. A partial single elemental microanalysis was performed on the final product. The results of the analysis were carbon 64.12 percent, hydrogen 4.86 percent, and sulfur 8.01 percent. The theoretical quantities of the elements present in the compound were carbon 64.66 percent, hydrogen 4.65 percent, nitrogen 14.37 percent, oxygen 8.20 percent, and sulfur 8.22 percent.

Synthesis of the Dye Complex

The dye complex was readily formed by addition of nickel-(II) chloride or the ultraviolet radiation stabilizer, previously described, to an ethanol solution of the dye ligand. The mixture formed may be separated by chromatographic development using an aluminum oxide adsorbent and absolute ethanol for elution. Chromatograms, made by using nickel-(II) chloride or the stabilizer as the source of nickel, indicated the presence of a single type of complex. In both cases, the complexes produced have similar retention times and color. A sample of the complex formed in ethanol was obtained by chromatography using nickel chloride as the metal donor. The sample was filtered through Celite and crystallized from

absolute ethanol from which a low yield of black, needle-like crystals was collected.

Although the dye complex was readily synthesized, as described above, determination of the spectra of this compound in 2,2,4-trimethylpentane proved to be difficult. This is due to the fact that the solubility of the complex in 2,2,4-trimethylpentane was low and that the compound had a strong tendency to be adsorbed by glass.

In an effort to acquire a spectrum of the complex in 2,2,4-trimethylpentane, a solvent interchange was attempted. This was performed by addition of 1.5, 1.0, and 0.5 milliliters of a concentrated absolute ethanol solution containing a known amount of the dye complex to 13 milliliters of 2,2,4-trimethylpentane. Spectra were taken of the solutions and one milliliter of absolute ethanol added to each. Spectra were taken again and another one milliliter sample of ethanol added. This procedure was continued until four milliliters of ethanol had been added. Plots of absorbancy at specific wave lengths versus concentration of ethanol were made and extrapolated to zero concentration ethanol. The absorbancy values obtained were used to construct an absorbancy versus concentration plot for the complex in pure 2,2,4-trimethylpentane. Results were extremely erratic; however, a general positive deviation from Lambert-Beer's law was indicated.

Because difficulty was encountered in obtaining the spectra of the dye-nickel-(II) complex in 2,2,4-trimethylpentane, and because some experimental evidence indicated that the compound obtained as described above might not be the same compound formed in 2,2,4-trimethylpentane, (refer to page 39) an alternate approach was sought whereby the relative stability

of the dye complex could be calculated. A process of iteration could be used in which a sample of the dye ligand in 2,2,4-trimethylpentane containing an excess amount of the stabilizer complex was assumed to have coordinated completely to give the dye complex. Spectral data of this sample could be used to calculate the concentration of the dye complex in a solution containing relatively equal amounts of dye ligand and stabilizer complex. From this data relative stability constants could be calculated and used to calculate the amount of unreacted dye ligand in the sample which had originally been assumed to have completely reacted. In this way, successively better evaluations of the relative stability of the dye complex could be achieved (refer to page 47).

Instrumentation

Optical measurements were made on a Beckman model DU spectrophotometer. The instrument was equipped with a constant voltage power supply and photomultiplier. The photomultiplier was used for all measurements. The one centimeter cells used were constructed of Corex; the five centimeter cells used were Vycor. The Vycor cells were used for measurement in the ultraviolet region. Although this was not the recommended material for working in this region, spectra of solvent blanks showed that the cells were sufficiently matched to allow their use. Transmittance values were read rather than absorbancy since estimation of the final digit was easier on the linear scale. Transmittance values were read to three significant figures and were transformed to absorbancy values by the use of tables.

Because the amount of material synthesized and purified was small, weighings were made on a low capacity, precision balance. The balance used was an August Sauter torsion balance with a ten milligram maximum. Weighings could be made to three significant figures.

Chemical Structure of the Metal Complexes Formed in Polypropylene Dyeing

Experimental Investigation of Dye Complexes

The method of continuous variations, or Job's method, can be used to determine the composition of a metal complex (refer to page 18). The method is based upon the assumption that only one complex, $M(Ll)_n$, is formed. Considering the system formed by addition of (1-v) volumes of a solution of the metal ion at concentration M_o, and v volumes of a solution of the ligand (Ll) at concentration $(Ll)_o$, it has been shown (23) that if $M_o = (Ll)_o$ the following equation applies.

$$n = \frac{v_{max}}{1-v_{max}} \qquad (19)$$

The volume v at which the concentration of $M(Ll)_n$ is maximal is v_{max}. The value of v_{max} may be readily obtained by measuring optical absorbancy of samples in which the value of v is allowed to vary from zero to one. It should be noted that the value of v is equal to the mole fraction of the ligand when $(Ll)_o = M_o$. At v_{max} a change in the optical properties of the samples occurs at wave lengths at which the ligand and complex have different absorbancy indexes.

A Job diagram using N,N-dimethylformamide as the reaction solvent was made. The initial concentration of the dye ligand and nickel ion was 2.50×10^{-5}M. Five, four and one-half, four, three and one-half, three, two and one-half, and one milliliters of dye solution were added respectively to zero, one-half, one, one and one-half, two, two and one-half, and four milliliters of solution containing nickel-(II) chloride. Measurements were made after the samples had been heated to 80°C for five

minutes and allowed to return to room temperature. The samples maintained constant spectra after the heating process. Absorbancy measurements were made at 25 millimicron intervals from 650 to 525 millimicrons. All the values of v_{max}, one at each wave length, fell within 0.570 and 0.580. Data for two of the wave lengths used are represented in Figure 7 (refer to page 41). Using equation (19) and the value of v_{max}, which was 0.575, the value of n was calculated to be 1.35. This indicates that a mixture of 1:1 - and 2:1 - complex is probably formed.

A two-phase modification of Job's method (refer to page 18) was used to study the complexes which might be formed in the polypropylene fiber. Three, four, five, six, seven, eight, and nine milliliters samples of a 3.00×10^{-6}M purified dye solution in 2,2,4-trimethylpentane were added respectively to seven, six, five, four, three, two and one milliliters samples of a 3.00×10^{-6}M nickel-(II) chloride solution in redistilled water. The nickel chloride solution also contained 0.1 percent of a pH 7.2 buffer, composed of equivalent weights of monosodium and disodium phosphate, and 0.1 percent of sodium chloride as an ionic strength control. To all of the samples containing more than five milliliters of dye solution, sufficient buffer solution containing phosphate salts and sodium chloride at the concentrations described above was added to make the volume of the two phases equal. A final sample of ten milliliters of the dye solution and ten milliliters of buffer solution, containing no nickel ion, was prepared. The small amount of buffer and ionic strength control used was due to the fact that metallic impurities present in the reagent grade chemicals would have been significant if higher concentrations were used.

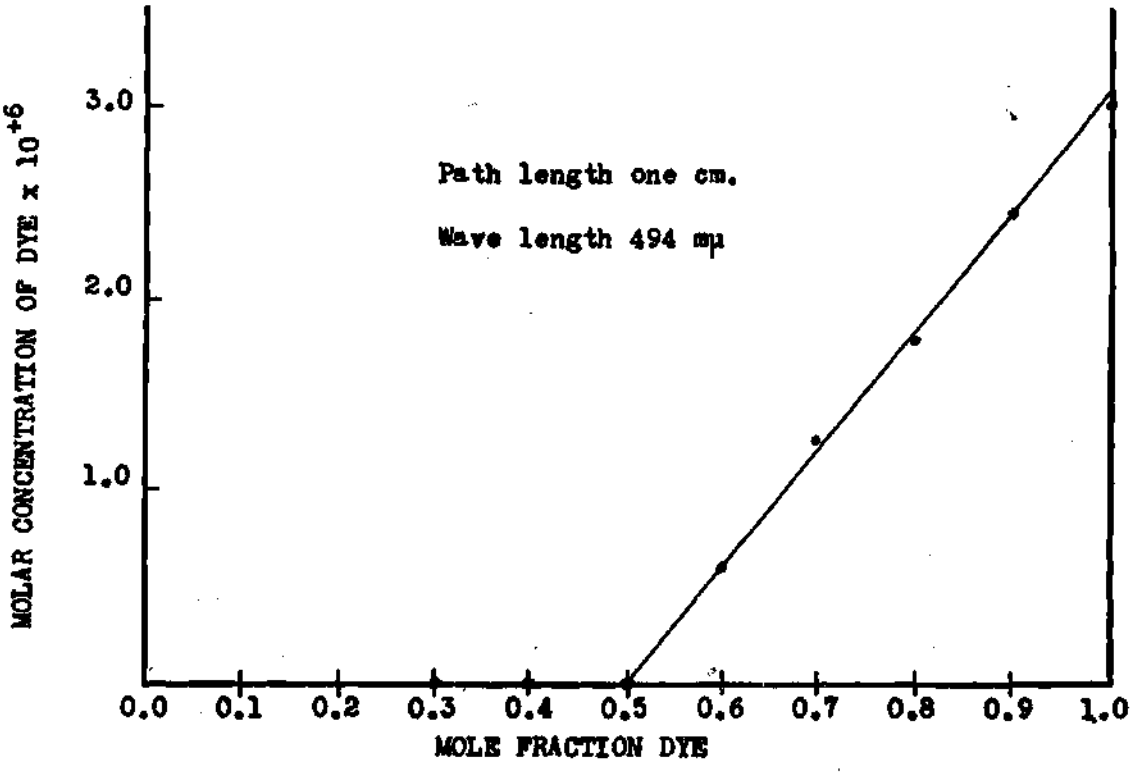


Figure 7. Aqueous - 2,2,4-trimethylpentane (two phase) Job Diagram of the Polypropylene Dye.

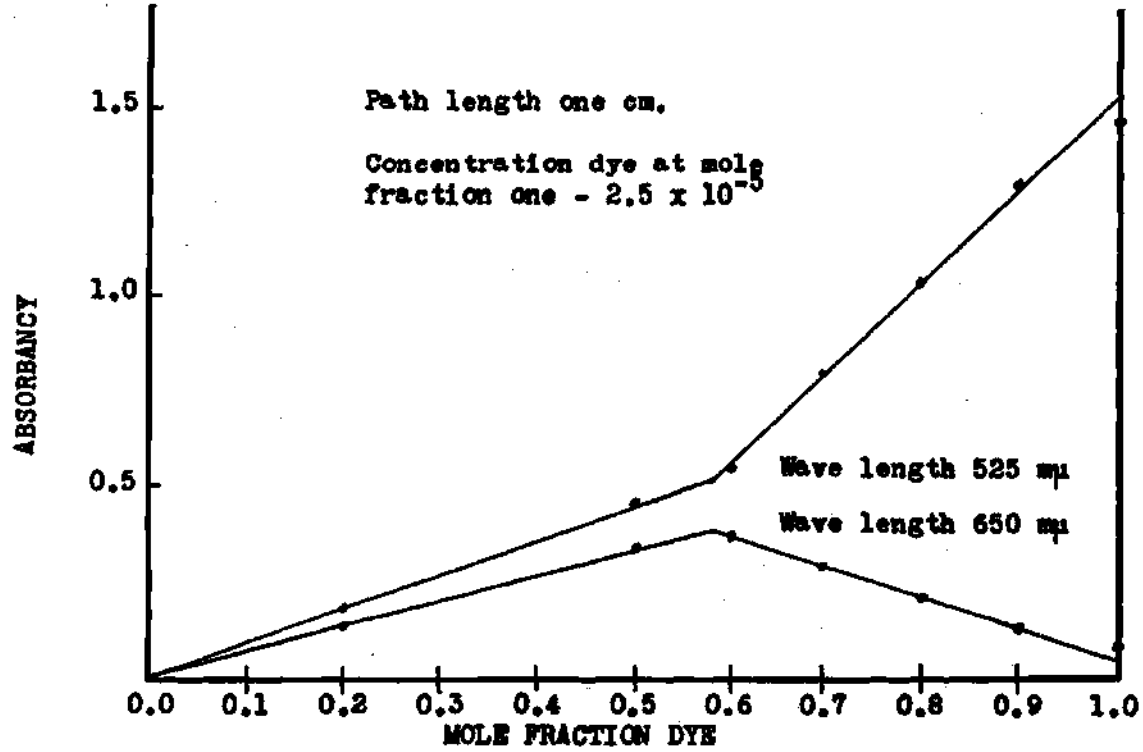


Figure 8. Job Diagram of the Polypropylene Dye in N,N-Dimethylformamide.

The two-phase mixtures were placed in tightly sealed vials and heated for 24 hours at 80°C with periodic shaking. The aliphatic upper layer of the reaction mixture was analyzed for the concentration of the dye by optical absorbancy measurements at 454 millimicrons. The complex was adsorbed by the walls of the glass container; and therefore, did not appear in the spectra. The values of the dye concentration, obtained from Figure 7 (refer to page 41), were plotted versus the mole fraction of the dye present in the mixture. The value of v_{max}, which was 0.50, indicated that the 1:1-complex was formed.

Discussion of the Structure of Complexes Formed in Polypropylene Dyeing in View of Experimental Results

The number of possible complexes formed between polypropylene dyes of the metalizable dispersed type and nickel-(II) is quite large. Nickel-(II) may exhibit coordination numbers of four and six. It appears that four-coordinate planar complexes are readily converted into six-coordinate octahedral complexes (24). The dye has the capability to act as a monodentate, bidentate, or terdentate ligand. Acting as a terdentate ligand, the dye may coordinate to give two distinct configurations. As depicted in Figure 9 and Figure 10 (refer to page 43), the dye could conceivably form two five-membered rings or a four and a six-membered ring depending upon the configuration of the azo group. Which form predominates will, of course, depend upon the relative energy of stabilization of the sets of rings formed, and perhaps upon some steric effect which is not made evident in a two-dimensional representation of the complex. If the dye molecule acts as a bi-dentate ligand, it probably does so by coordination at the hydroxy group and azo nitrogen rather than at the heterocyclic

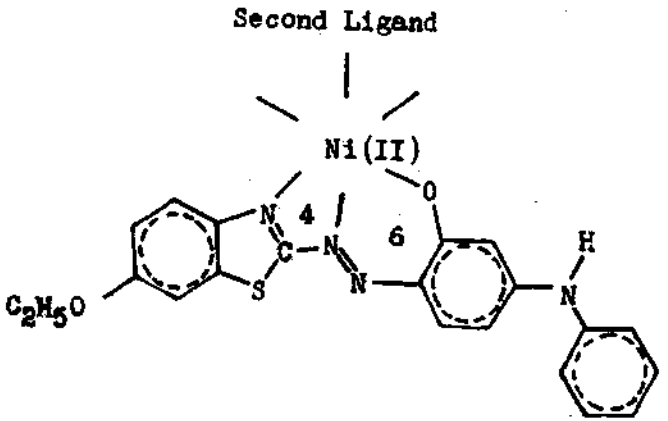


Figure 10. Dye in 4,6 Configuration.

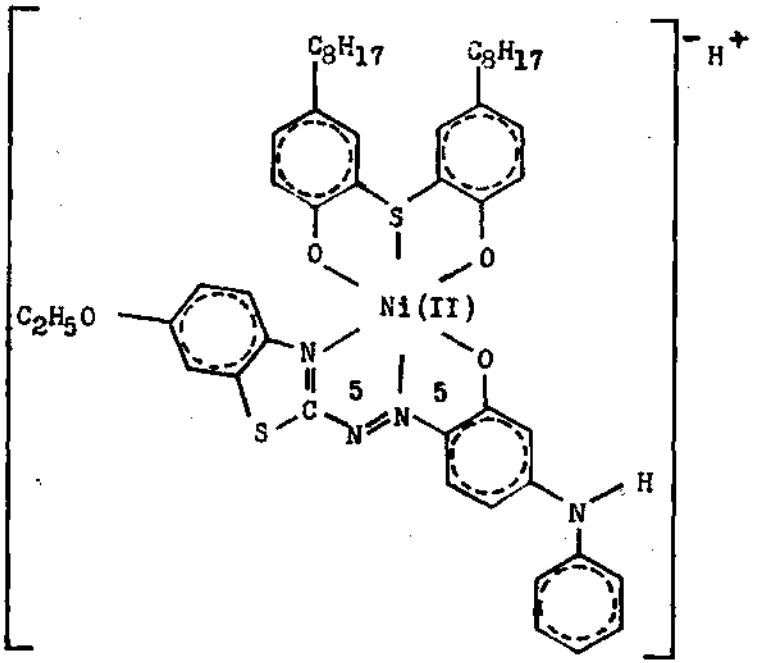


Figure 9. Mixed Complex, with Dye Ligand in 5,5 Configuration.

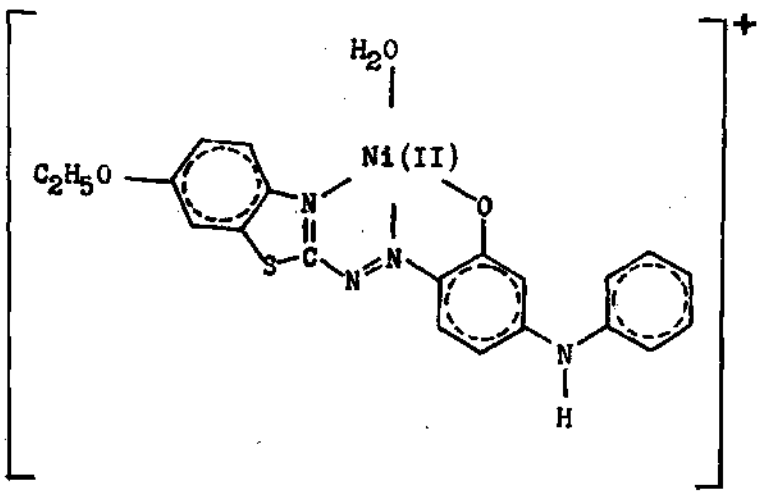


Figure 11. Possible Structure of 1:1-Complex.

nitrogen and azo nitrogen, since in the former case, a more stable six-membered ring may be formed.

In the Job diagrams, both 1:1- and 2:1-complexes have been indicated to be formed. A possible structure of the 1:1-complex is shown in Figure 11 (refer to page 43). Although water is depicted as the monodentate ligand, any nucleophile present in the solution would suffice. It should be noted that the complex as shown carries a positive charge.

In the medium in which relative stability measurements were made (anhydrous 2,2,4-trimethy,pentane), the initial species present were the stabilizer complex and the dye ligand (refer to page 20 and 21). If one proposes the formation of a 1:1-complex of the dye in this medium and writes the balanced equation for such a reaction, it is found that the strongest nucleophile in solution and the only species which would maintain electrical neutrality of the complex would be 4-(1,1,3,3-tetramethylbutyl)-2-[1-hydroxy-4-(1,1,3,3-tetramethylbutyl)phenylthio] phenoxy ion. It may be proposed that the four-coordinate complex of the dye and this phenoxy ion would readily convert into the six-coordinate complex depicted in Figure 9. This complex is merely the mixed complex M(St)(D) (refer to page 9 and 21). In summation, it may be said that 1:1-complexes are probably not formed by the species under investigation in anhydrous 2,2,4-trimethylpentane.

From the practical standpoint, it should be added that, as indicated by the above discussion, in the actual dyeing system a large number of complexes could be formed. If the complexes formed had significantly different spectra, dulling of the final shade would occur. For this reason, elucidation of the structure of the complexes formed might aid in synthesis

of dyes which give bright colors, when applied separately or in mixtures.

Measurement of the Relative Stability of the Dye Complex in Anhydrous 2,2,4-trimethylpentane

Preliminary Measurements

The spectra of all of the reaction species obtained by synthesis are given in Figure 12 (refer to page 46). The spectra of the stabilizer complex and stabilizer ligand was terminated below 250 millimicrons because the solvent began to absorb below this wave length. The stabilizer complex and stabilizer ligand exhibited negligible absorbancies beyond 475 millimicrons, even at concentrations as high as 2×10^{-4} M in the stabilizer complex. This meant that wave lengths from 475 millimicrons to 700 millimicrons could be used in determination of relative stability constants.

The spectrum of the dye ligand in anhydrous 2,2,4-trimethylpentane was taken at wave lengths from 450 to 700 millimicrons at 25 millimicron increments. The concentrations of the orange-colored solutions used for establishing the absorbancy versus concentration plot are in Figure 13 (refer to page 48). Due to the abnormal deviation from Lambert-Beer's law, which was indicated by the first set of data, a second set of data was acquired. The second set of data is given in Figure 13; and the circles, indicated on the parts of the graph in which they would not cause confusion, are sufficiently large to encompass both sets of data.

The solution of maximum concentration shown in the figure is approximately one-third saturated. This was determined by adding an ample amount of the purified dye to a sample of anhydrous 2,2,4-trimethylpentane under reflux. Needle-like, reddish-brown crystals formed rapidly upon cooling. The mixture was allowed to stand for 48 hours at 25°C. From the rate of

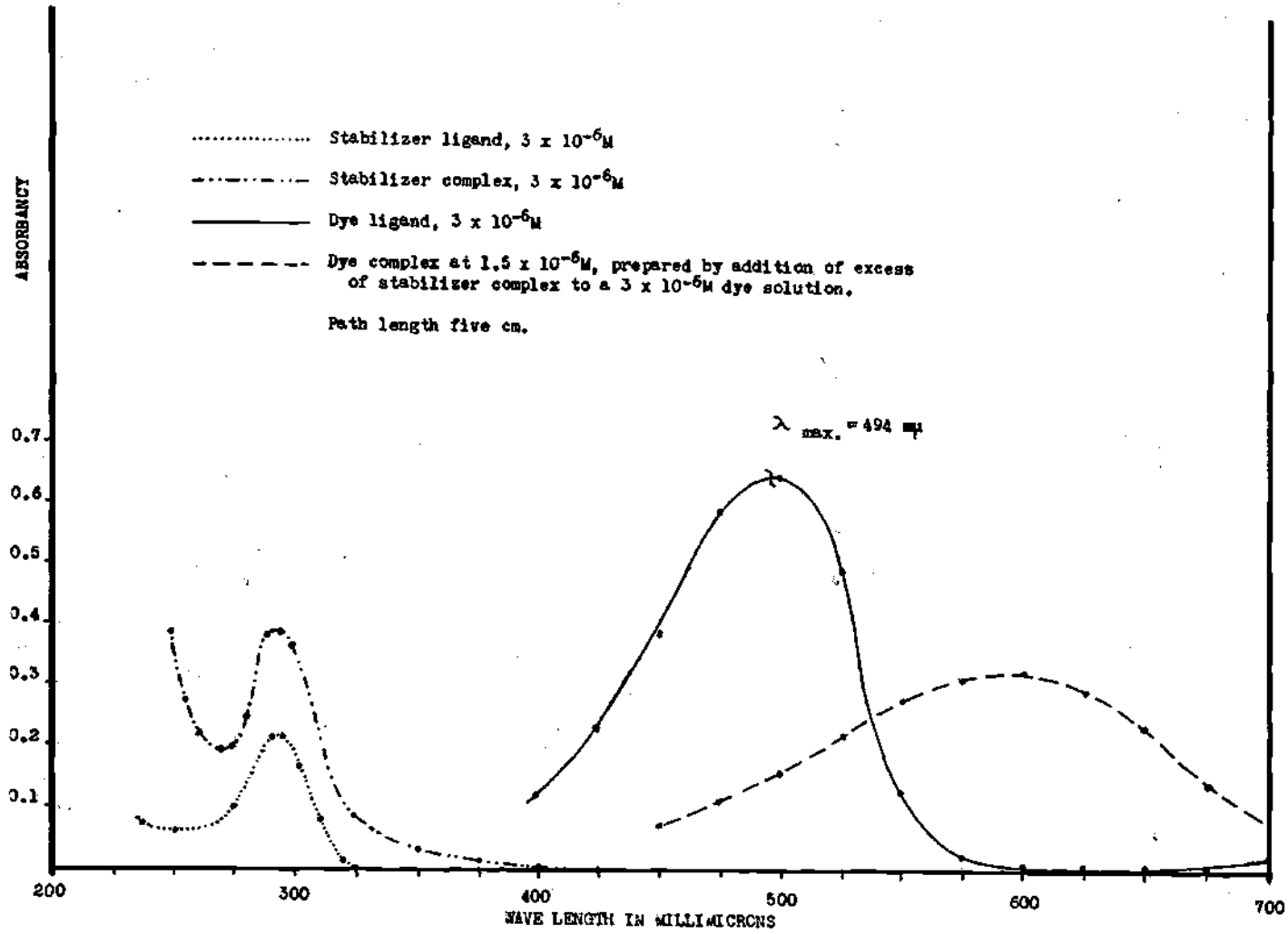


Figure 12. Spectra of Reaction Species in 2,2,4-trimethylpentane.

growth of the crystals, this amount of time seemed ample to establish equilibrium. The solution formed was analyzed optically by diluting to a concentration below 3×10^{-6}M and calculating the concentration by the use of Figure 13. The saturated solution was 9.2×10^{-6}M in dye.

The initial spectra of the dye complex (refer to page 38) was obtained by analyzing a solution which was 7.43×10^{-5}M in stabilizer complex and 3.00×10^{-6}M in dye ligand. The solution was maintained at room temperature and diluted to the concentrations (formation of the 2:1 complex was assumed for calculation of molar concentration) indicated in Figure 14 (refer to page 49). After the samples were prepared they were placed in the cell and heated to 80°C for 30 minutes. This was done to minimize the error caused by sorption on the walls of the volumetric flasks and pipettes. The samples maintained constant spectra after heating. Under magnification, crystal form was not indicated by the material absorbed by the glass.

Considerable scatter was encountered in the data. This is probably due to sorption of the complex on the walls of the cell. Only the points for the wave length equal to 675 millimicrons are plotted in Figure 14. This was done because if all the data points were included the graph would be confusing. The data used in the construction of the graph is reproduced in tabular form in Table 2 (refer to page 67). It should be noted that the points for the wave length of 675 millimicrons gave the worst agreement with linearity.

Iteration Procedure

As discussed previously (refer to page 38), an iteration procedure may be used to calculate the relative stability of the dye complex. This

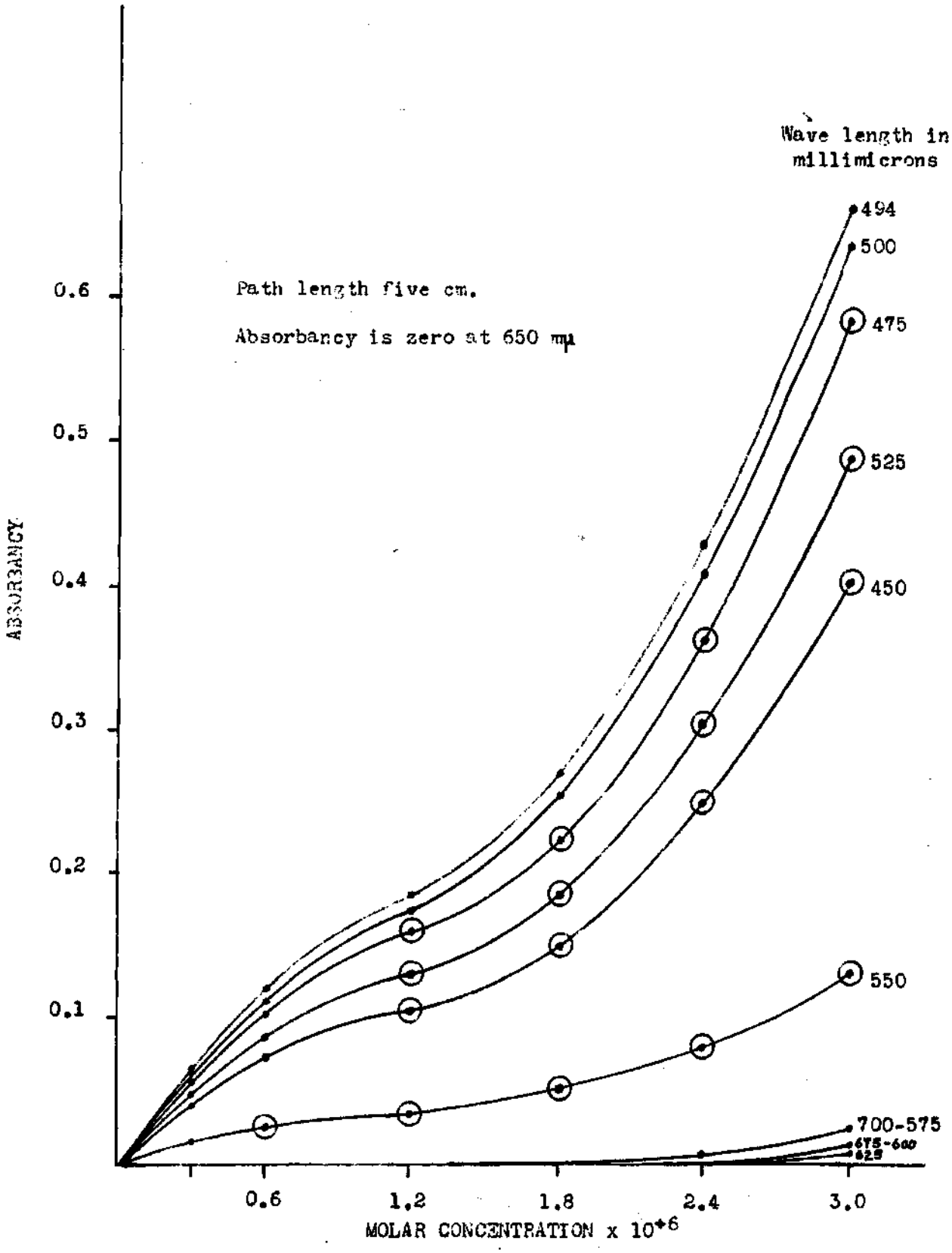


Figure 13. Absorbancy Versus Concentration Plot for the Dye in 2,2,4-trimethylpentane.

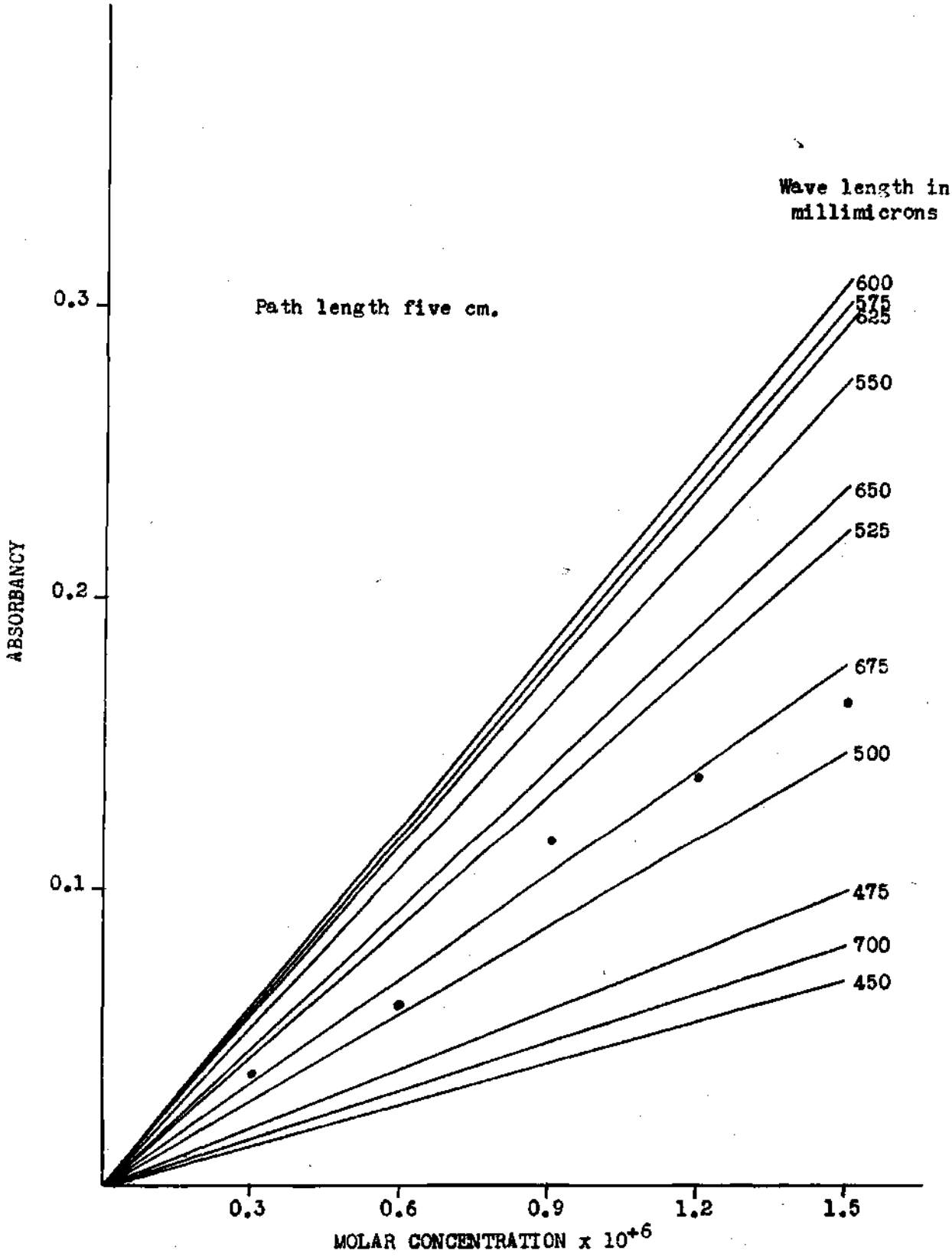


Figure 14. Absorbancy Versus Concentration Plot for the Dye-nickel-(II) Complex in 2,2,4-trimethylpentane.

is not the ideal method of measurement. It would be best if all of the probable reaction species could be prepared in their pure form and their spectra taken. In this way the concentration of each could be measured in a reaction mixture at equilibrium and at many wave lengths. The concentration of each specie calculated at each wave length should be the same. If the concentrations proved to be dependent upon the wave length, a reaction specie which has not been accounted for might be present (25).

The calculation of equilibrium constants may readily be achieved under the assumption that Lambert-Beer's law applies to all species in the solution (refer to page 17). However, this assumption is not justifiable in the system under investigation. Calculation of the relative stability constants using iteration or the synthesis of all the reaction species simply requires the solution of a set of simultaneous equations.

At equilibrium, the reaction may be indicated as follows:

$$M(St)_2 + (D) \underset{}{\overset{(K_{21})_{St,D}}{\rightleftharpoons}} M(St)(D) + (St)$$

$$M(St)_2 + 2(D) \underset{}{\overset{(K_{22})_{St,D}}{\rightleftharpoons}} M(D)_2 + 2(St)$$

For these equilibria, the equilibrium constant, $(K_{21})_{St,D}$, is the stability of the mixed dye-stabilizer complex relative to the stabilizer complex; and the equilibrium constant, $(K_{22})_{St,D}$, is the stability of the dye complex relative to the stabilizer complex (refer to page 26).

From the manner in which the initial reaction solution was prepared, the total molar concentration of metal $[M_T]$, of stabilizer ligand $[St_T]$, and of dye ligand $[D_T]$ are known. Letting brackets represent molar

concentrations and using the above symbolism, the following equations are obtained.

$$[M_T] = [M(St)_2] + [M(St)(D)] + [M(D)_2] \quad (20)$$

$$[St_T] = [St] + [M(St)(D)] + 2[M(St)_2] \quad (21)$$

$$[D_T] = [D] + [M(St)(D)] + 2[M(D)_2] \quad (22)$$

These three equations contain five unknowns. The other two equations required for solution of the set could be readily obtained from total absorbancy measurements at any two wave lengths, providing the absorbancy of each specie present was known at each wave length.

Using the iteration process, it is necessary to assume that no mixed complex is formed, that $(K_{22})_{St,D}$ is independent of concentration, and initially that the spectral relationships, given in Figure 14, are those of the pure 2:1 dye complex. Under these assumptions the value of $(K_{22})_{St,D}$ may be calculated for a solution in which the concentration of both dye ligand and dye complex are similar.

If the mixed complex is not formed, equations (20), (21), and (22) reduce to equations (23), (24), and (25)

$$[M_T] = [M(St)_2] + [M(D)_2] \quad (23)$$

$$[St_T] = [St] + 2[M(St)_2] \quad (24)$$

$$[D_T] = [D] + 2[M(D)_2] \quad (25)$$

In all the solutions prepared, the stabilizer complex is the only source of the stabilizer ligand. In this case, the total concentration of metal must be one-half the concentration of the stabilizer ligand (symbolically written $2[M_T] = [St_T]$). Using this relationship, equation (26) may be obtained from equations (23) and (24).

$$[St] = 2[M(D)_2] \tag{26}$$

From the law of mass action, the equilibrium reaction for formation of the 2:1 dye complex may be written as follows:

$$(K_{22})_{St,D} = \frac{[M(D)_2][St]^2}{[M(St)_2][D]^2} \tag{27}$$

Using equations (26), (23), and (25), equation (27) may be reduced to the following equation.

$$(K_{22})_{St,D} = \frac{[M(D)_2]^3}{\{[M_T]-[M(D)_2]\}\{\frac{1}{2}[D_T]-[M(D)_2]\}^2} \tag{28}$$

This equation is used by iteration to calculate the value of $(K_{22})_{St,D}$. An outline of the iteration procedure is given in the appendix (refer to page 68).

An anhydrous 2,2,4-trimethylpentane solution, which was initially 1.50×10^{-5}M in stabilizer complex and 3.00×10^{-6}M in dye ligand, was prepared and heated for one hour at 80°C. The constant spectra was taken of the solution at 24°C. The spectra is given in Figure 15 (refer to page 53) and in Table 1 (refer to page 54).

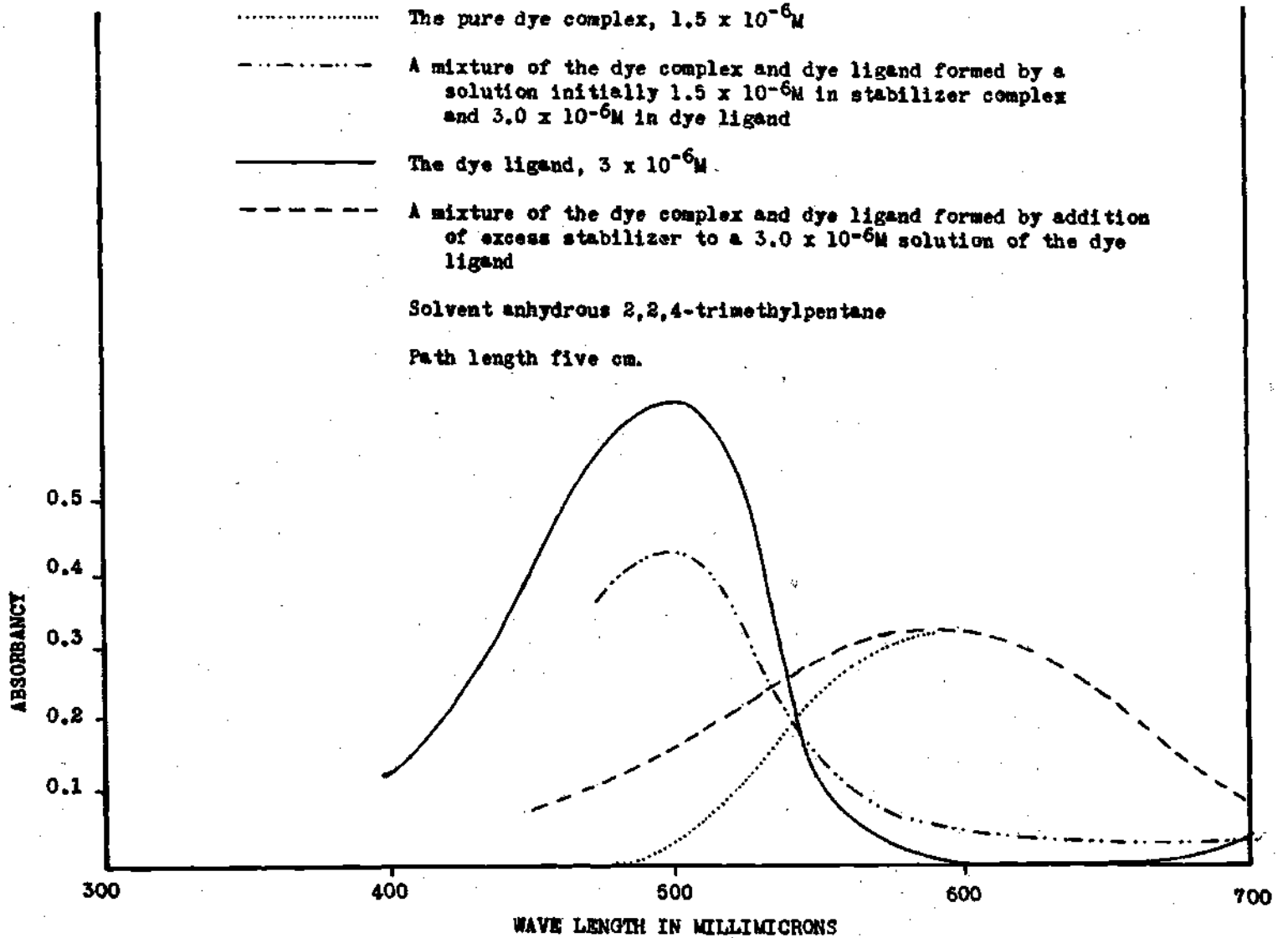


Figure 15. Spectra of the Species used in the Iteration Procedure.

Table 1. Values of the Relative Stability Constant of the Dye Complex

λ Wave Length in Millimicrons	A Absorbancy of Solution Under Analysis	$(K_{22})_{St,D}$ Relative Stability Constant of the Dye Complex
700	.0209	.00137
675	.0246	.00095
650	.0269	.00170
625	.0315	.00315
600	.0410	.00410
575	.0809	.00462
550	.1487	.0192
525	.3143	.0250
500	.4260	.0188
475	.3768	.0156

CHAPTER III

DISCUSSION OF RESULTS

The iteration was performed independently at each wave length from 475 to 700 millimicrons. The results were tabulated in Table 1 (refer to page 54).

One of the original assumptions which made calculation of the relative stability constants possible was that no mixed dye-stabilizer complex was formed. If this assumption were true, it would be reasonable to expect the values of $(K_{22})_{St,D}$ to be the same at each wave length (refer to page 50). As seen in Table 2, this was not the case. However, it was difficult to determine whether this fluctuation was due to formation of the mixed complex or to the inaccuracy in measurement, caused by adsorption of the dye complex by glass.

Another assumption used in calculation of $(K_{22})_{St,D}$ was that this constant was independent of concentration of the species in solution. In this respect it should be mentioned that no ionic strength or hydrogen ion control was included in the solvent. Ionic strength in anhydrous 2,2,4-trimethylpentane was essentially controlled by the solvent system at zero. It should also be noted that the reaction of the stabilizer complex and the dye ligand was balanced in hydrogen ion. For this reason, it was assumed that control of the pH was not required.

Knowledge of the value of $(K_{22})_{St,D}$ allowed the construction of the true spectrum of the dye complex in 2,2,4-trimethylpentane. This was included in Figure 15. This spectra was constructed by the use of the

value of the arithmetic mean of the values calculated for $(K_{22})_{St,D}$ from wave lengths of 500 to 700 millimicrons. The value of this average was 0.0094.

CHAPTER IV

CONCLUSIONS

The blocking phenomenon, as it applies to the polypropylene metalizable disperse dyeing system, has been defined. An equilibrium model for the dyeing system has been proposed and relationships, consisted with this model, which would aid in the study of blocking have been obtained. On the basis of this model, it has been shown that variables unique to the metalizable dispersed dyeing system are the rate of formation of the dye complex, the stability of the dye complex, and the solubility of the dye complex in the fiber phase. It has been assumed that the fiber phase may be simulated by 2,2,4-trimethylpentane for the measurement of these variables.

1. It has been shown that the measurement of over-all stability constants may not be made in anhydrous 2,2,4-trimethylpentane. However, in this media, the stability of a complex involved in a replacement reaction may be measured relative to a reference complex. The knowledge of the relative stability of two dissimilar complexes with a third complex, as the reference complex, is sufficient to calculate the stability of the two dissimilar complexes relative to each other. The stabilizer complex was chosen as the reference complex.

2. In 2,2,4-trimethylpentane saturated with water, a 1:1-complex of nickel-(II) and 6-ethoxy-2-(2-hydroxy-4-anilinophenylazo)-benzothiazole is formed. However, it has been shown that the 2:1-complex of the above compounds does exist in other solvent media.

3. Reasons that the 1:1-dye-metal complex is not formed in anhydrous 2,2,4-trimethylpentane have been discussed. The relative stability of the 2:1-dye-metal complex has been determined in anhydrous 2,2,4-trimethylpentane, under the assumptions that no mixed dye-stabilizer complex or 1:1-dye-metal complex had been formed. The values obtained are tabulated on page 54.

CHAPTER V

RECOMMENDATIONS

To prove or disprove the model presented and to determine its relation to blocking phenomenon, an experimental study of the kinetics and equilibrium of the polypropylene metalizable disperse dyeing system must be made. Ideally, sets of dyes should be chosen which do and do not exhibit blocking. These dyes should be of different color since this will aid in the measurement of the extent of blocking which has occurred. In this way a relatively small group of dyes can be used to establish the validity of the equilibrium model proposed or to determine whether kinetic variables are the most important factors. Logical choice of the dyes, for which stability, solubility, and lability measurements should be made, will minimize the task of elucidation of the dyeing mechanism.

In anticipation of such a program, the values of the molar absorbancy indexes in absolute ethanol solution of the dye-nickel complex and the dye ligand were determined. The data for these determinations is given in Figure 16 (refer to page 72). The values of the molar absorbancy index of the dye-nickel complex were 8.6×10^4 at 600 millimicrons and 6.9×10^4 at 525 millimicrons. The complex was formed by addition of nickel-(II) chloride in excess to the ethanol solution of the dye ligand. The values of the molar absorbancy index of the dye ligand were 7.0×10^3 at 600 millimicrons and 4.9×10^4 at 525 millimicrons (based on the gram molecular weight of the dye which was 390.472). These values may be used to establish the purity of the commercial dye mixture for use in dyeing experiments.

Measurement of the rate of formation of the dye complex in 2,2,4-trimethylpentane should be relatively easy to perform. It was noted that in this research the labile nature of the ligand was depressed in 2,2,4-trimethylpentane. Formation of the complex in this solvent required approximately 15 minutes at 80°C; where as, the same species in a solvent such as ethanol or N,N-dimethylformamide usually required only five to ten minutes, even at room temperature.

Determination of the solubility of the dye complex in pure 2,2,4-trimethylpentane will probably be difficult. In the first case, it must be clarified whether one is interested in the removal of the compound from solution by adsorption on glass or by precipitation. It might be possible to measure the solubility of the complex in 2,2,4-trimethylpentane containing progressively smaller amounts of absolute ethanol. It may then be justifiable to extrapolate this data to zero concentration of ethanol.

Measurement of the stability of the complexes was hindered by deviation from Lambert-Beer's law and by adsorption of the complex on glass. This could be overcome by the use of a better solvent. The author suggests the use of anhydrous ethanol. It has been found (refer to page 72) that the dye ligand and dye complex obey Lambert-Beer's law in this solvent. It may be proposed that the over-all stability of the dye complex and the stabilizer complex might be affected to a proportional extent by a change in the solvent. In this case, the relative stability of the dye complex, which is the value desired, would be unaffected. This assumption can readily be proved or disproved by measurement of the values of the relative stability of the dye, used in this research work, in absolute ethanol.

The author also suggests that a study be made on whatever solvent is chosen for future work to determine the effect of trace amounts of water on the composition of the complex formed. This could be done by performing Job diagrams in which progressively larger amounts of water are present. This would aid greatly in the evaluation of the structure of the complexes formed in a practical dyeing system.

Another interesting aspect, which is not directly connected with dyeing metalizable disperse dyes but which might merit investigation, is the ultraviolet radiation stability of the fiber after dyeing. Patent literature (26) indicates that the stabilizer ligand alone affords no protection to polypropylene; only when nickel is present does a protective effect exist. This brings up the question, after dyeing with a sufficiently large amount of the dye to essentially exhaust the dye sites, what protects the fiber from degradation? If the dye complex acts as the ultraviolet radiation stabilizer after dyeing, this would indicate that dyeing of the fiber, containing relatively inexpensive nickel salts of organic acids, might simultaneously produce polymer stabilization and coloration. It might also suggest that radiation protection of dyeings of pastel shades on fibers containing nickel salts of organic acids might be improved by incorporation of the non-colored ligand, such as o,o'-bis-(p-1,1,3,3-tetramethylbutyl)phenol monosulfide, to the dyebath.

The fact that the stabilizer ligand affords no optical protection to the polymer does not mean that its presence is not beneficial to the dyeing operation. On the contrary, (p-1,1,3,3-tetramethylbutyl)phenol has been used as a carrier for application of disperse dyes to polypropylene (27). It would appear from this evidence that the stabilizer ligand might

act as a plasticizer for the polymer and greatly accelerate diffusion of the dyes into the substrate.

APPENDIX

GLOSSARY OF ABBREVIATIONS

i	Denotes the i^{th} dye used in a dye mixture, i = 1,2,3,4,....,w
j	Denotes the j^{th} dye used in a dye mixture, j = 1,2,3,4,....,m and $j \neq i$
k_{di}	The rate constant associated with the rate of dissociation of the i^{th} dye complex
k_{fi}	The rate constant associated with the rate of formation of the i^{th} dye complex
k_{si}	The rate constant associated with the rate of diffusion of the i^{th} dye into the substrate
n	A subscript used to denote the number of ligands associated with a given central metal ion
p	The number of positive charges associated with a given metal ion
q and r	The number of negative charges associated with a given ligand
t_m	The reproduced time used as standard in dye compatibility tests
v_{max}	The volume of ligand solution required to obtain a breakpoint in a Job diagram
w	The number of dyes used in a dye mixture
x	The number of metal ions required to form a given complex
y	The number of ligands (L1) required to form a given complex
z	The number of ligands (L2) required to form a given complex
B_{xyz}	The over-all stability constant for formation of the $M_x(L1)_y(L2)_z$ complex (defined on page 16)
$(B_{120})_{L1}$, $(B_{120})_{St}$, and $(B_{120})_{Di}$	--- The over-all stability constant for formation of the $M(L1)_2$, $M(St)_2$, and $M(D_i)_2$ complexes respectively
$(B_{102})_{L2}$, $(B_{102})_{Dj}$, and $(B_{102})_{Di}$	--- The over-all stability constant for formation of the $M(L2)_2$, $M(D_j)_2$, and $M(D_i)_2$ complexes respectively

$(B_{111})_{L1,L2}$, $(B_{111})_{St,Di}$, $(B_{111})_{St,Dj}$, and $(B_{111})_{Di,Dj}$ --- The over-all stability constant for formation of the M(L1)(L2), M(St)(D_i), M(St)(D_j), and M(D_i)(D_j) mixed complexes respectively

$B_{1(N-n)n}$ The over-all stability constant for formation of the $M(L1)_{N-n}(L2)_n$ complex

B_{1NO} The over-all stability constant for formation of the $M(L1)_N$ complex

C_i A constant defined on page 10

D Any polypropylene metalizable disperse dye ligand

D_{Di} The dye i, used in a mixture, which remains in aqueous dispersion at equilibrium

D_{fi} The dye i, used in a mixture, which is precipitated or fixed in the fiber

D_{fT} The total of the dyes, used in a mixture, which are fixed in the fiber = $\sum_{i=1}^{w} D_{fi}$

D_{Ii} The dye i, used in a mixture, which was initially dispersed in the dyebath

D_{IT} The total of the dyes, used in a mixture, which were initially dispersed in the dyebath = $\sum_{i=1}^{w} D_{Ii}$

D_i The i^{th} dye ligand dissolved in the fiber phase

Di A subscript used to denote the i^{th} dye ligand

D_j The j^{th} dye ligand dissolved in the fiber phase

Dj A subscript used to denote the j^{th} dye ligand

D_{Ri} The dye i, used in a mixture, which has reacted with the dye sites at equilibrium

D_{RT} The total of the dyes, used in a mixture, which has reacted with the dye sites at equilibrium = $\sum_{i=1}^{w} D_{Ri}$

D_S The dye sites present in the fiber which by convention are twice the initial concentration of nickel in the fiber. This is true since 2:1-complexes are considered to be formed

D_T The total amount of dye ligand present in the solution in its coordinated and un-coordinated forms

FE_i The fixation efficiency of the i^{th} dye used in a mixture $\equiv D_{fi}/D_{Ri}$

K_i The equilibrium constant for the formation of the 2:1-dye complex from the stabilizer complex and the dye ligand = $(K_{22})_{St,Di}$

$(K_{21})_{L1,L2}$ --- The stability of the M(L1)(L2) complex relative to the $M(L1)_2$ complex, where (L1,L2) may be (St,Di), (St,Dj), (St,D), or (Di,Dj)

$(K_{22})_{L1,L2}$ --- The stability of the $M(L2)_2$ complex relative to the $M(L1)_2$ complex, where (L1,L2) may be (St,Di), (St,Dj), (St,D), or (Di,Dj)

(L1) The first of two dissimilar ligands

(L2) The second of two dissimilar ligands

M The metal ion available for coordination

$M(D)_2$ The 2:1-complex of a polypropylene metalizable disperse dye

$M(D_i)_2$ The 2:1-complex of the i^{th} dye used in a mixture

$(M(D_i)_2)_{sat}$ --- The concentration of a saturated solution of the i^{th} dye complex in the fiber phase

$M(D_i)(D_j)$ --- The mixed complex formed between two dyes i and j used in a mixture

$M(D_j)_2$ The 2:1-complex of the j^{th} dye

$M(L1)_N$,$M(L1)_n$ --- A complex formed by coordination with N and n ligands respectively

$M(L1)_2$ The 2:1-complex of the first of two ligands

$M(St)_2$ The stabilizer complex

M(St)(D), $M(St)(D_i)$, $M(St)(D_j)$ --- The mixed complex formed by coordination of a stabilizer ligand and a dye ligand with a single central metal ion

M_T The total amount of metal present in the solution in its coordinated and un-coordinated forms

$M_x(L1)_y(L2)_z$ --- The complex formed by coordination of x atoms of M, y molecules of (L1), z molecules of (L2)

N A subscript used to denote the number of ligands associated with a given central metal ion

St The stabilizer ligand

St_T The total amount of stabilizer ligand present in the solution in its coordinated and un-coordinated forms

$\left(\frac{d(D_{fi})}{dt}\right)_D$ --- The rate of desorption of dye i

$\left(\frac{d(D_{fi})}{dt}\right)_S$ --- The rate of sorption of dye i

$\left(\frac{d(D_{fi})}{dt}\right)_T$ --- The over-all rate of sorption of dye i, or the rate of build-up of the i^{th} dye

( ) Used to group symbols, or to indicate concentration in moles per kilogram of fiber

[ ] Used to indicate concentration in moles per liter of solution

Table 2. Absorbancy Values for the Dye-Nickel-(II) Complex, Formed by Addition of Excess Stabilizer Complex, in 2,2,4-trimethylpentane at Various Wave Lengths and Concentrations.

Wave Length in Millimicrons	Molar Concentration of the Dye Ligand				
	1.5×10^{-6}M	1.2×10^{-6}M	0.9×10^{-6}M	0.6×10^{-6}M	0.3×10^{-6}M
700	.0804	.0630	.0506	.0353	.0250
675	.1649	.1403	.1180	.0600	.0386
650	.2381	.2000	.1331	.1029	.0482
625	.2950	.2403	.1599	.1221	.0521
600	.3206	.2479	.1778	.1273	.0570
575	.3028	.2351	.1778	.1221	.0550
550	.2757	.2255	.1549	.1129	.0895
525	.2219	.1838	.1249	.0931	.0400
500	.1487	.1192	.0862	.0701	.0292
475	.1051	.0783	.0630	.0501	.0223
450	.0706	.0605	.0458	.0301	.0155

EXAMPLE OF THE INTERATION PROCEDURE

The relative stability constants for formation of the dye complex were calculated manually by iteration. The iteration required the use of equations (25) and (28) of Chapter II (refer to pages 51 and 52). For clarity these equations are rewritten.

$$(K_{22})_{St,D} = \frac{[M(D)_2]^3}{\{[M_T]-[M(D)_2]\}\{\frac{1}{2}[D_T]-[M(D)_2]\}^2} \qquad (1)$$

$$[D_T] = [D] + 2[M(D)_2] \qquad (2)$$

For the case in which the concentration stabilizer complex is initially very high, the following approximation applies,

$$[M_T]-[M(D)_2] \tilde{=} [M_T] \qquad (3)$$

Using this approximation, for the solution used in preparation of Figure 14 (refer to page 49), equation (1) reduce to equation (4). For easy reference during iteration, it was found beneficial to plot the value of $\log(K_{22})_{St,D}$ (given by this equation) versus the values of $M(D)_2$ from zero to 1.5×10^{-5}

$$(K_{22})_{St,D} = \frac{[M(D)_2]^3}{[M_T]\{\frac{1}{2}[D]-[M(D)_2]\}^2} = \frac{[M(D)_2]^3}{7.43 \times 10^{-5}\{.150 \times 10^{-5}-[M(D)_2]\}^2} \qquad (4)$$

For the solution, analyzed with the aid of Figure 13 and Figure 14, the concentration of $[M_T]$ was purposely made equal to $\frac{1}{2}[D_T]$. Using this

restriction in equation (1), a more easily handled equation (5) results.

$$(K_{22})_{St,D} = \left(\frac{[M(D)_2]}{\frac{1}{2}[D_T] - [M(D)_2]} \right)^3 \qquad (5)$$

The iteration procedure for the wave length of 525 millimicrons, at which the absorbancy of the solution under analysis was A = 0.3143 (obtained from Table 1, page 54), was as follows:

The first cycle of the iteration gave the following results.

The concentration of the dye ligand in the solution under analysis, which agreed with equation (2) and with the value of A = .3143, was found. This was determined graphically with the aid of Figure 13 and Figure 14 (refer to pages 48 and 49). This gave the following result.

$$[D] = .215 \times 10^{-5} M$$

The concentration of the dye complex in the solution under analysis was calculated by using the value of [D], given above, and equation (2). This gave the following result.

$$[M(D)_2] = .042 \times 10^{-5} M$$

The value of $(K_{22})_{St,D}$ was calculated by using the value of $M(D)_2$, given above, and equation (5). This gave the following result.

$$(K_{22})_{St,D} = .059$$

The concentration of the dye complex in the solution, initially assumed to be $.15 \times 10^{-5}$M in pure complex, was calculated by using the

value of $(K_{22})_{St,D}$, given above, and equation (4). This gave the following result.

$$[M(D)_2] = .102 \times 10^{-5}M$$

The concentration of the dye ligand in the solution, initially assumed to be $.15 \times 10^{-5}M$ in pure complex, was calculated by using the value of $[M(D)_2]$, given above, and equation (2). This gave the following result.

$$[D] = .096 \times 10^{-5}M$$

The absorbancy, due to the presence of the dye ligand at the wave length 525 millimicrons in the solution (initially assumed to be $.150 \times 10^{-5}M$ in pure complex), was obtained by using the value of [D], as given above, and Figure 13 (refer to page 48). This gave the following result.

$$A = .120$$

Graphic correction for the presence of free dye ligand in Figure 14 (refer to page 49) was made. The second cycle of the iteration, performed identically to the first cycle, gave the following results.

$$[D] = .232 \times 10^{-5}M$$

$$[M(D)_2] = .034 \times 10^{-5}M$$

$$(K_{22})_{St,D} = .0250$$

$$[M(D)_2] = .089 \times 10^{-5} M$$

$$[D] = .122 \times 10^{-5} M$$

$$A = .130$$

Graphic correction for the presence of the dye ligand in Figure 14 was repeated.

The third cycle of the iteration was then begun. The first result was found to be as follows:

$$[D] = .232 \times 10^{-5} M$$

From this point this iteration was repetitive.

It was found that for the wave lengths from 575 to 700 millimicrons, the iteration was essentially complete in a single cycle. This was due to the low absorbancy of the dye ligand at these wave lengths. It was also found that for wave lengths of 500 and 475 millimicrons a preliminary guess of very low absorbancy index for the dye complex would make calculations possible.

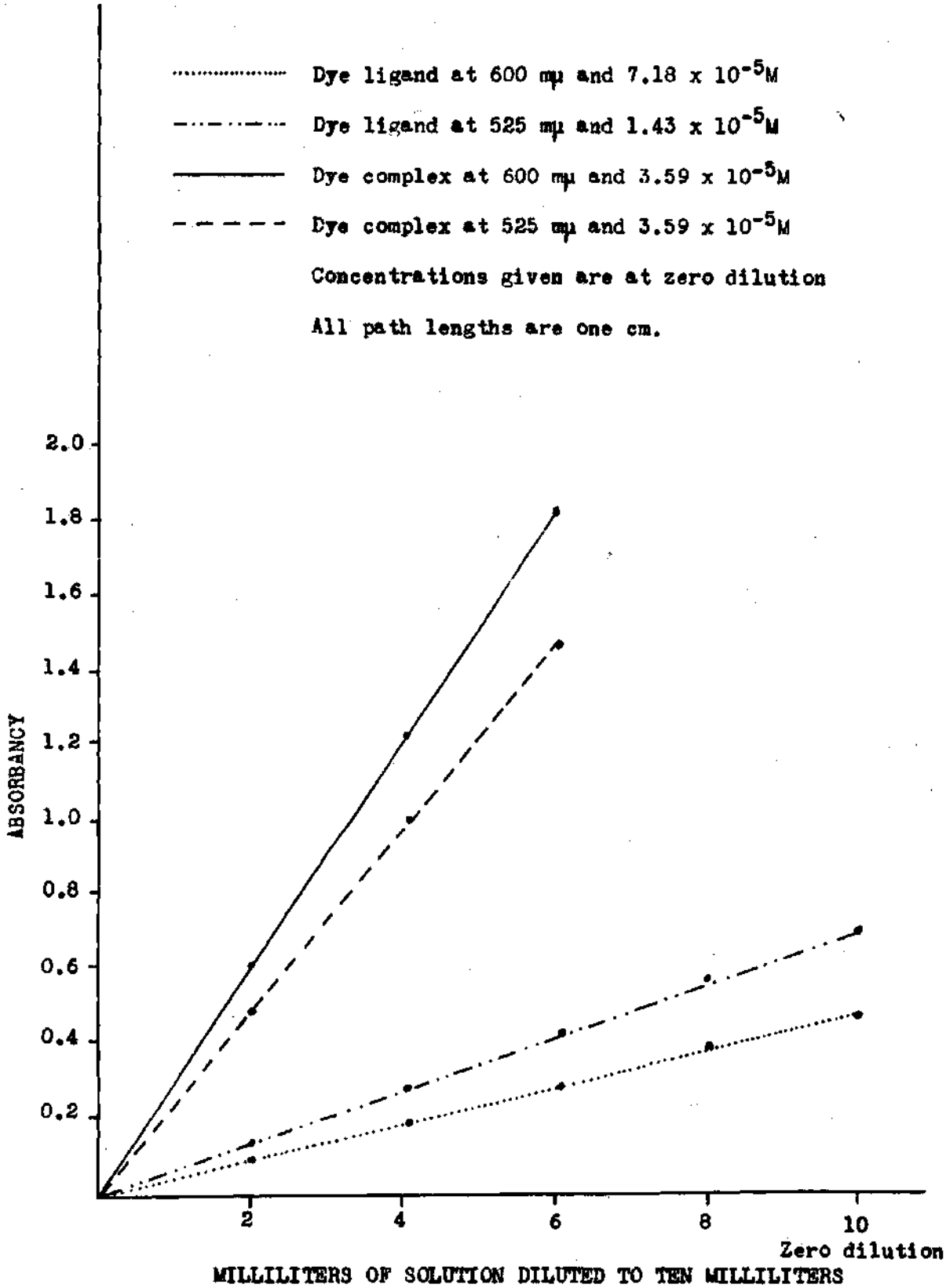


Figure 16. Absorbancy Versus Concentration Plot for the Dye and Dye-nickel-(II) Complex in Absolute Ethanol.

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